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NUMBER TWO

RUBBER CHEMISTRY AND TECHNOLOGY

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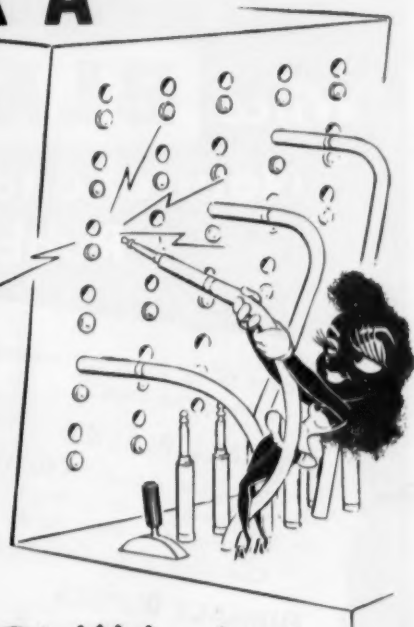
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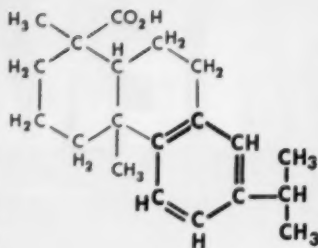
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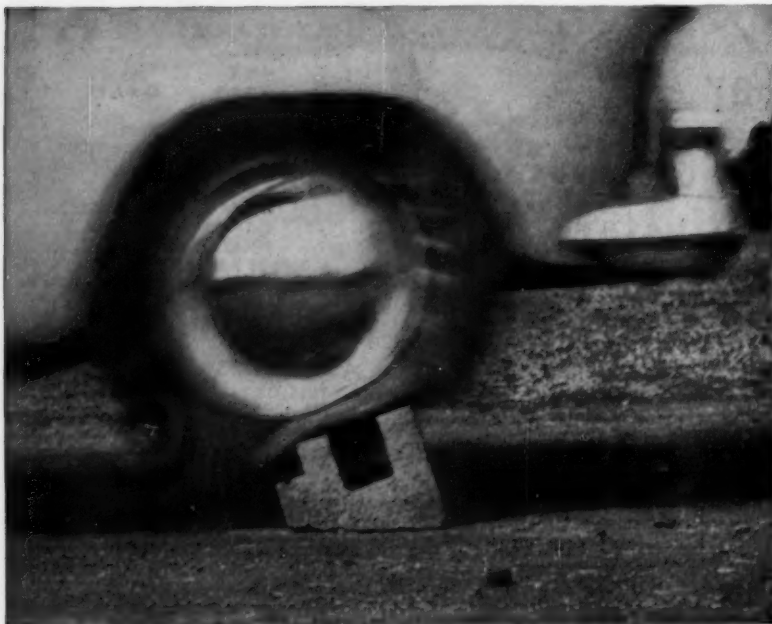


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FUTURE MEETINGS

The Division of Rubber Chemistry of the American Chemical Society is scheduled to hold meetings in the following cities in 1955, 1956, and 1957.

<i>Meeting</i>	<i>City</i>	<i>Hotel</i>	<i>Date</i>
1955 Spring	Detroit*	Sheraton-Cadillac	May 4-6
1955 Fall	Philadelphia*	Bellevue-Stratford	November 2-4
1956 Spring	Cleveland*	Cleveland	May 16-18
1956 Fall	Atlantic City	—	September 19-21
1957 Spring	Montreal*	Sheraton-Mt. Royal	May 15-17
1957 Fall	New York	—	September 11-13

* The meeting will be held independent of, and at a different time from, the corresponding spring or fall meeting of the American Chemical Society.

NEW BOOKS AND OTHER PUBLICATIONS

THE SERVICES RUBBER INVESTIGATIONS. Published by H. M. Stationery Office, Atlantic House, Holborn Viaduct, London, E. C. 1, England. Available from British Information Services, 30 Rockefeller Plaza, New York 20, N. Y. 6 × 9½ in. 324 pp. \$5.75.—Rubber technologists will recall the series of "Manufacturers' Memoranda" and "Users' Memoranda" which were issued, during and subsequent to World War II, in England by the Services Rubber Investigations Panel. These memoranda were compiled by, and largely based on, investigations conducted by the Rubber Laboratories of Imperial Chemical Industries, Ltd., which were headed at the time by W. J. S. Naunton. This book is a revised collection of the "Users' Memoranda".

The book is divided into nine chapters: (1) Properties of Synthetic Rubbers and Rubberlike Materials; (2) Aging, Heat, and Oil Resistance of Natural and Synthetic Rubbers at Elevated Temperatures; (3) Natural and Synthetic Rubbers at Low Temperatures; (4) Natural and Synthetic Rubbers as Engineering Materials; (5) The Shrinkage of Natural Rubber in Molding; (6) Creep Phenomena of Natural and Synthetic Rubbers; (7) Effect of High Grade Aviation Fuels on Synthetic Rubbers; (8) Hardness Measurements of Natural and Synthetic Rubbers; (9) Identification and Determination of Natural and Synthetic Rubbers. Author and subject indexes are provided.

A good deal of useful information for rubber chemists and technologists is to be found in this new book, which is a welcome addition to the rubber literature. Whereas the earlier memoranda were restricted somewhat in distribution, the present collection is available to the entire industry. [From the *Rubber Age* of New York.]

DETERIORATION OF MATERIALS. Edited by Glenn A. Greathouse and Carl J. Wessel. Published by Reinhold Publishing Corp., 430 Park Ave., New York 22, N.Y. 6 × 9 in. 836 pp. \$12.00.—Prepared with the collaboration of 24 specialists, this book describes and analyzes the causes of deterioration in materials and presents proven techniques for preventing or retarding such deterioration. Divided into four sections, it covers the climatic, chemical, physical, and biological agents of deterioration and the prevention of deterioration in metals, wood, paper, textiles, leather, plastics, rubber, paint, and many other materials. The four sections are: (1) Some Important Factors in Deterioration; (2) Materials and Their Preservation; (3) Some Assembled Units and Their Preservation; (4) Some Special Aspects of Preservation. Included is a 60-page chapter devoted to plastics and rubber, prepared by Albert Lightbody. Merritt E. Roberts and C. J. Wessel (one of the editors), which contains 150 literature references. The chapter covers the nature of high polymers, types of polymers, the effect of compounding, and plasticizers. The causes of deterioration in numerous types of plastics and in both natural and synthetic rubbers are outlined and preventive techniques discussed. [From the *Rubber Age* of New York.]

PIONEER AND PACEMAKER. The Firestone Tire & Rubber Co., Akron, O. 64 pages.—This is the story of the growth of The Firestone Tire & Rubber Co. from its inception in 1900, when a working force of 12 began producing solid rubber tires for horse-drawn carriages, to its present world-wide organization, employing 80,000 people and manufacturing goods worth more than a billion dollars a year. Profusely illustrated with photographs of men and machines, this booklet relates the company's history and describes every phase of its daily operation, from the cultivation of Liberian rubber to the after-hours' recreational activities of Firestone employees. [From the *Rubber World*.]

SPECIFICATIONS FOR SCRAP RUBBER. Revised January 25, 1955. The Rubber Reclaimers Association, Inc., New York, N. Y. 4 pages.—Superseding specifications issued January, 1954, these contain minor wording changes in paragraphs relating to foreign scrap, packages, claims, and standard grades. [From the *Rubber World*.]

A STUDY BY INFRARED SPECTROGRAPHY OF THE REACTION KINETICS OF THE AGING OF NATURAL RUBBER. II. EXPERIMENTS ON THE EFFECT OF LIGHT *

A. TRÁČ AND V. KELLÖ

DEPARTMENT OF PHYSICAL CHEMISTRY, TECHNICAL HIGH SCHOOL, BRATISLAVA,
CZECHOSLOVAKIA, IN COLLABORATION WITH THE RESEARCH INSTITUTE OF
CABLES AND INSULATION, BRATISLAVA

Many rubber products are exposed to the influence of light, either direct or scattered, during service. In the presence of atmospheric oxygen, light brings about changes in the physical properties of both vulcanized and unvulcanized natural rubber, ordinarily with degradation of quality. The surface of such products becomes sticky, inelastic, brittle, or even cracked, the electric resistance of the surface decreases rapidly, the loss angle increases, and the tensile strength decreases progressively. All these changes are concerned in the notion of the "aging" of rubber. If ozone is present in addition to atmospheric oxygen during exposure to light, the changes are much more rapid.

Many authors have studied the active spectral range of solar radiation, mercury light, and electric lamps. For example, Kröger and Staude¹ proved that rubber shows highest absorption (Figure 1) in the range of 2000–2500 Å. Bateman² established that, during exposure to ultraviolet light, the short-wave ultraviolet range is most active up to about 3700 Å, although, in the range from 2700 to 2800 Å, a perceptible decrease of effectiveness is observed. The total effect in the range from 2200 to 3700 Å shows a quantum number of the order of 10^{-4} .

Asano³ assumed that radiation longer than 3100 Å has no significant influence and that changes in rubber are much more rapid at wave lengths between 2000 and 2250 Å. With vulcanized rubber, the shorter the wave length and the higher the temperature, the greater is the effect of light, as also appears from measurements by Yamazaki⁴. According to his measurements, the effect of light at a wave length over 4300 Å is very weak, with the exception of over-vulcanized rubber.

Experiments by Pummerer⁵, who studied the formation of photogels in rubber solutions during exposure to light, show that the effective light is of shorter wave length than 3150 Å. According to other experiments made by him, direct solar radiation is just as effective as the light of a mercury quartz lamp. According to Bondy⁶, the active component of solar light which governs oxidation lies between 3000 and 4800 Å. His results lead to the conclusion that solar and ultraviolet light are equally effective, although ozone is formed only at short wave lengths which are not present in sunlight. Some authors do not agree fully with the opinion that tests of light aging artificially accelerated are an exact criterion of the stability of rubber in sunlight, although others offer tests with ultraviolet light as a good relative indication⁷ of the

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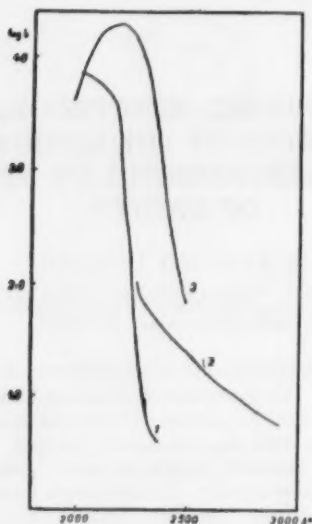


Fig. 1.—Absorption. 1. Sol rubber. 2. Uncoagulated latex. 3. Isoprene.

resistance of crude and vulcanized rubber to sunlight under ordinary natural conditions. The differences between the effect of sunlight and a mercury quartz lamp were studied by Weightman⁸, who established that a violet carbide arc is very similar to sunlight in its effect.

As we stated in a previous article⁸, our light source was a mercury quartz tube. In Table I, the principal lines in the wave-length range from 2224.7 to 2534.8 Å and the most intense lines up to 7371.7 Å are shown. The relative intensities according to Brode¹⁰ are also given.

The line at 2536.5 Å is given as well; this does not appear in the spectrum of high-pressure radiation, owing to autoabsorption. The intensities of the separate lines are by no means equal in each case, and, as is known, they depend

TABLE I

Å	Relative intensity
2224.7	30
2247.6	30
2378.3	20
2848.8	30
2534.8	30
2536.5	1000
3131.5	300
3650.1	5000
3662.9	400
3663.3	400
4046.6	300
4358.4	500
5460.7	1000
5789.7	500
5790.6	1000

on the pressure of mercury vapor in the tubes used. The relation between the aging process and the second mercury tube used will be discussed later in Part IV.

Changes caused by the action of light in the structure of rubber are very diverse. Rubber is depolymerized¹¹; on the other hand, ultraviolet radiation promotes the polymerization of isoprene and styrene¹². Rubber solutions exposed to sunlight or ultraviolet light in an inert atmosphere form gels¹³, while rubber in solution in ordinary solvents becomes insoluble¹⁴ as a result of the formation of side chains, which indicates vulcanization.

Bernstein¹⁵ vulcanized rubber in solution in the presence of sulfur by exposing the solution to radiation from a mercury lamp. Vulcanization by ultraviolet light can usually be effected¹⁶ in 4-8 minutes at 20-90° C. The rubber must be irradiated in a vacuum or in an inert gas, in order to prevent its destruction¹⁷. In the presence of protective red or yellow dyes, rubber can also be vulcanized in air¹⁸. Stern¹⁹ assumed that vulcanization is a phenomenon coincident with depolymerization. According to Burghardt²⁰, light can damage vulcanized rubber only in the presence of other destructive agents, chief of which are oxygen and ozone.

It has long been known that rubber exposed to light undergoes significant structural changes, due to the influence of oxygen²¹. A large number of works are concerned with the oxidative destruction of rubberlike polymers. The great changes in the physical and chemical properties of natural and vulcanized rubber during exposure to sunlight or ultraviolet radiation in air or in the presence of oxygen have been studied by various methods²². Shortening of the chains of the polymer is reflected by the decrease of viscosity of rubber solutions²³.

Unvulcanized rubber becomes sticky in the presence of light, as work by Blake and Bruce²⁴ has shown; they determined the qualitative and quantitative relations between stickiness and oxygen absorption. A decrease of tensile strength and a decrease of elasticity is regarded as a measure of oxidation²⁵. Dogadkin and Panchenkov²⁶ studied the decrease of surface tension of rubber solutions exposed in air and in nitrogen to light. Aqueous extracts of rubber exposed to light reduce gold chloride to colloidal gold, whereas pale crepe not irradiated has no reducing properties. Dogadkin and Baladina²⁷ also studied the electric conductivity of the extract. After a slight initial decrease, it increased considerably.

Defries and Naunton²⁸ studied the influence of sunlight on the color of unvulcanized and vulcanized rubber mixtures. In the presence of oxygen²⁹, the effect of ultraviolet light was observed to lead to cyclization of the rubber.

Cole and Field³⁰ described the changes in the infrared spectrum of synthetic GR-S, observed during irradiation with ultraviolet light. At the same time, they studied the structural changes in natural rubber oxidized by heat. These changes are similar to those in GR-S, and are described in detail from a qualitative viewpoint.

In our experiments, changes in the structure of rubber during radiation were studied quantitatively. This analysis is not limited to an explanation of the mechanism of aging of rubber, but also presents a rather accurate picture of the mechanism of other reactions which can take place in rubber, as well as in other natural and synthetic polymers, and that several reactions may take place at the same time, or only one reaction, according to the experimental conditions. As will be shown later, this study of crude rubber provides an explanation of the mechanism of vulcanization and the problem of aging of vulcanized rubber.

QUALITATIVE CHANGES IN THE INFRARED SPECTRUM OF CRUDE RUBBER

Figure 2 shows the spectrum of a natural pale crepe rubber, which had been extracted for 7 hours with acetone, and also the spectrum of this rubber after irradiation for 1550 minutes in air at a distance of 18 cm. at 25° C. The following changes were observed in the spectrum: the zone with maximum at 11.95 μ ,



characteristic of the isoprene group, $-\text{CH}_2-\overset{\text{CH}_3}{\underset{|}{\text{C}}}=\text{CH}-\text{CH}_2-$, decreased sharply, indicating a considerable loss of original isoprene segments. The original low-intensity zone at 11.25 μ increases; this may indicate the formation of olefin groups of the type, $-\text{R}_2\text{C}=\text{CH}_2$, which are absorbed in this region. Here, however, the overlapping of the adjacent broad absorption band also has considerable influence. The new broad absorption band in the range between 11 and 7.5 μ (approximately after 10 μ) is due to the oscillation of the C—O—groups in the byproducts of the oxidation of rubber, and it can be attributed to acids, esters, or alcohols, as well as to ether bridges. If we assume that, accord-

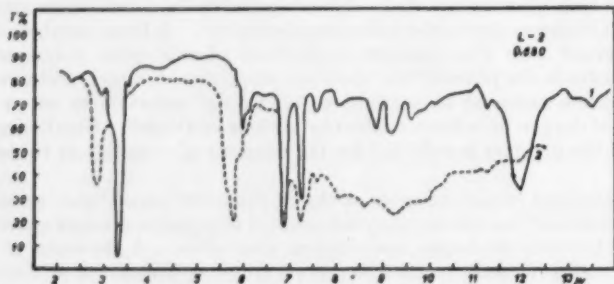


Fig. 2.—1. Pale crepe extracted 7 hours with acetone. 2. Pale crepe irradiated 1550 minutes in air (18 cm., 25° C).

ing to the experimental observation of Hilton²¹, in a heat-oxidized rubber (with 11 per cent bound oxygen) up to 35 per cent of the rubber is bound by ether bridges, we may presume that a part of the broad absorption band (about 8.5–9.2 μ) is due to the ether oxygen bridges.

Absorption in the range 9.8–10.5 μ most probably is due to $-\text{C}-\text{C}-$ groups. A study of this region would then provide more definite information about changes of the number of $-\text{C}-\text{C}-$ groups, which govern rupture, polymerization of the chains, and eventual formation of side chains. As is seen in Figure 3, the character of the broad absorption band depends on the conditions of irradiation in the range of 11–7.5 μ . This is evidence of the varying proportions of oxidative byproducts in the different stages of oxidation under differing experimental conditions.

The absorption zones of deformation oscillation of C—H of the bonds in the CH_2 and CH_3 groups decrease; this is the result of a decrease of isoprene segments. If we assume that, at the beginning, the double bonds decrease very slowly, and decrease rapidly only after longer exposure, we can assume also a considerable rupture of the polymer chains between the carbon atoms which are united by single bonds. The great changes, however, are due to the influence of the broad absorption band at 7.6–11 μ .

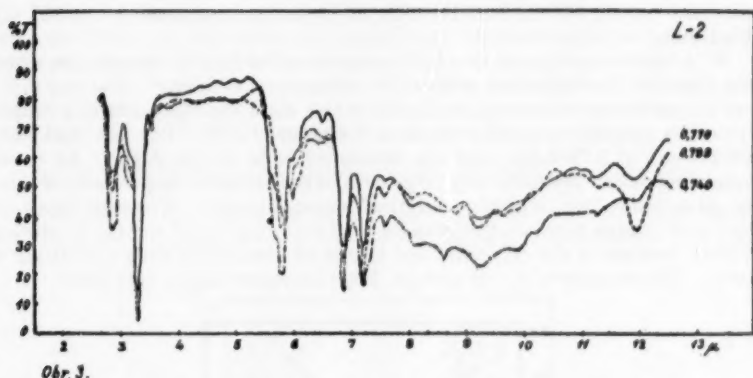


FIG. 3.—Pale crepe irradiated 200 minutes in air (3.5 cm., 55° C). Pale crepe irradiated 150 minutes (quartz cuvette, 11 cm., 25° C). Pale crepe extracted with methanol, irradiated 1570 minutes (14 cm., 38° C).

The intense range of about 5.79–5.82 μ is due to carbonyl groups, C=O, i.e., ketone, aldehyde, and carboxyl groups. This zone is formed by the fusion of a slightly pronounced doublet, which can be easily observed in a thick sheet of rubber which has not been irradiated; this indicates a slight initial oxidation (Figure 4). The absorption means are at 5.75 and 5.84 μ . After longer exposure, both zones unite to form a single zone centered at 5.80 μ at lower tem-

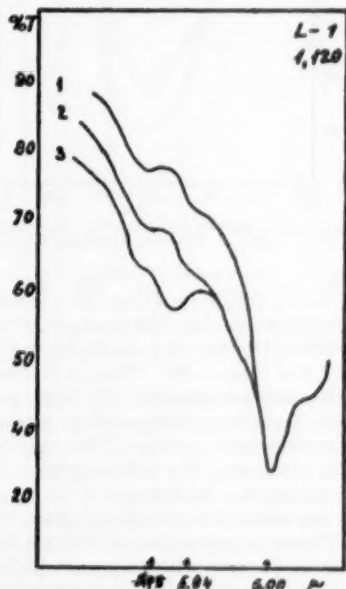


FIG. 4.—1. Pale crepe, not irradiated. 2. Pale crepe irradiated 30 minutes (18 cm., 27° C). 3. Pale crepe irradiated 80 minutes (18 cm., 27° C).

peratures (about 14° C) and at 5.82 μ at higher temperatures (over 30° C) (Figure 5).

With specimens exposed at a high temperature at 3.5 cm. distance, or, after long exposure, the beginning of the new zone appears at 5.66 μ . This may indicate the presence of unassociated acids, which show absorption in this range. The esters generally show absorption in the range of 5.71–5.79 μ , the aldehydes and ketones at 5.79–5.92 μ , and the associated acids at 5.75–5.88 μ . All these types of oxidation products may be present in the oxidation byproducts of rubber, as appears from Hilton's analytical measurements²¹. The absorption of the C=O groups conceals the changes of the absorption of the C=C groups (6.00 μ), because of the intensity, and this is an obstacle to their quantitative study. The number of C—H groups (3.3 μ) decreases only a very little.

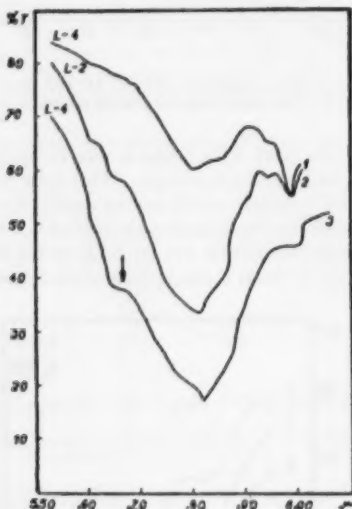


FIG. 5.—1. Pale crepe irradiated 2800 minutes (2.5 cm., 16° C; $E_b = 0.820$). 2. Pale crepe irradiated 2800 minutes (14 cm., 32° C; $E_b = 0.698$). 3. Pale crepe irradiated 621 minutes (2.5 cm., 62° C; $E_b = 0.769$).

The OH groups of the oxidation products are absorbed at 2.96 μ in an unexposed specimen. During oxidation, the number of such groups increases. With this increase, the absorption center is displaced toward higher oscillations, and reaches a value of 2.86 μ (Figure 6). This displacement can be caused by the transition of the OH groups associated with hydrogen bridges to unassociated groups as a result of absorption of energy during exposure. The character of the zone 2.96–2.98 μ remains unchanged. Thus, two types of OH groups are present in the oxidation products. We may, therefore, assume an increase of the new zone which is displaced. As is known²², in the range of 2.7–2.8 μ , the free OH groups absorb the associated groups at 2.98 μ . The two zones and the displacement might explain the prevalence of OH groups of strongly oxidized rubber over hydroperoxide groups, which appear chiefly at the beginning of oxidation, because the vibration of the OH groups is influenced by the adjacent bound atom, and by the oxygen in the hydroperoxide group (—O—O—H) and

the carbon in the hydroxyl group (—C—O—H). The difference between the mass of these atoms is, however, so small that this explanation of such a large displacement seems improbable.

In a future work the qualitative differences in the spectra of specimens oxidized in the presence of an accelerator by light, and heat-oxidized, which were studied by D'Or and Kössler²³, will be described.

QUANTITATIVE STUDY OF CHANGES OF INFRARED SPECTRA

Changes in the structure of rubber were studied with hard films. The films were exposed for a given time in air, and immediately thereafter

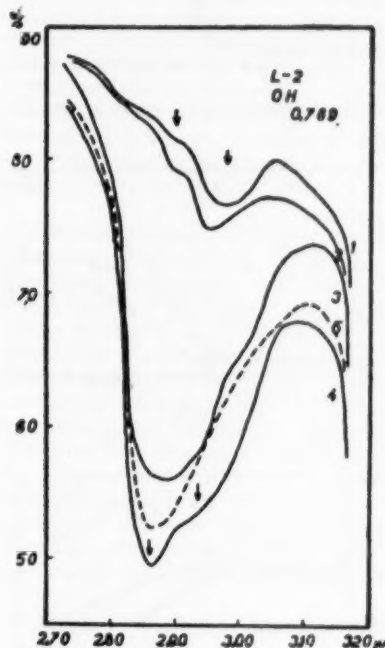


Fig. 6.—1. Pale crepe, not irradiated. 2. Pale crepe irradiated 30 minutes (14 cm., 30° C). 3. Pale crepe irradiated 80 minutes (14 cm., 30° C). 4. Pale crepe irradiated 200 minutes (14 cm., 30° C). 5. Pale crepe irradiated 2800 minutes (14 cm., 30° C).

the parts of the infrared spectrum in which changes appeared were studied. The increase of the O—H , C=O , and $\text{R}_2\text{C=CH}_2$ groups, the decrease of the CH_2 and CH_3 groups, the isoprene units of the polymer, and changes of the number of C=C bonds were studied. Changes in the range (about 10μ) in which oscillation of the C—C groups is assumed to take place were also investigated. The measured extinction value was corrected for scattering; the extinction value of the light scattered was subtracted from it. The values of $\Delta E = E_\lambda$ (exposed) and E_λ (unexposed) were drawn graphically. The time in logarithmic terms was represented on the abscissa and the characteristic extinction changes ΔE on the ordinate.

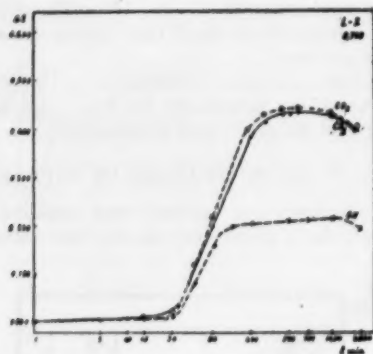


FIG. 7.—Pale crepe irradiated at 14 cm. distance at 30° C (O—H 2.86).

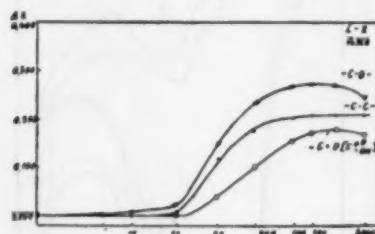


FIG. 8.

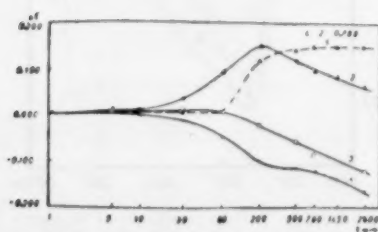


FIG. 9.

1. Vinyl group
2. CH_2 group

3. CH_2-CH_2 groups
4. Isoprene group

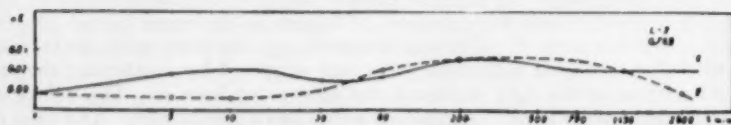


FIG. 10.

1. Scattering

2. $\text{C}=\text{C}$ -group

The shape of these curves for a single atomic group in the same specimen is shown in Figures 7, 8, 9, and 10.

Most of the specimens were exposed for about 400–500 minutes, beyond which the curves no longer changed. The longest measurements were after 2800 minutes; these showed that, by exposure, the shape of the reaction curves are influenced relatively little by the experimental conditions, e.g., intensity and temperature. However, after very long exposure, or very intense irradiation at high temperatures, there were slight decreases of the C=O, O—H, C—O, C=O (carboxyl), and O—H groups. The zone at 10μ , which we attribute to the —C—C groups, either does not change (average distance of source) or increases slightly (close to the source, with effective cooling), while the neighboring vinyl groups (with a lower number of oscillations) do not change, and the broad absorption at high oscillations (9μ) decreases. The zone corresponding to the isoprene units and the CH_2 , CH_3 , and CH_2 groups likewise broadens. In many cases the curves show no further change after 150–200 minutes. In studying aging and its characteristic reaction mechanism, the part of the curve after the leveling off is most important.

For a detailed study of oxidation, we chose, as the chief criterion, measurements of the increase of the C=O and OH groups, since the changes in the zones of these groups follow the changes in the zones of the other groups on the whole quite regularly.

The oscillation spectrum of atmospheric water vapor was used in the calibration of the wave lengths. This makes it possible to study the increase of the C=O groups at an absolutely constant wave length. Since the center of the zone of C=O groups remained dependent on the experimental conditions at values of 5.80μ to 5.82μ , we studied the change of the extinction value at both points. It was observed that the curves which represent the change of both extinction values, although they have the same form, differ in height and course at various stages of oxidation. The curve for the extinction of the 5.80μ zone begins to ascend rapidly, but, during exposure at a distance of 14 cm., the curve for 5.82μ intersects the curve for 5.80μ and reaches somewhat higher values in the constant segment. During exposure to a close source of radiation, and after cooling, the curve of 5.82μ is lower than the curve of 5.80μ during the whole reaction, but at 60°C it is always higher. In the diagrams, the zone of 5.82μ is designated by CO_{11} and the zone at 5.80μ by CO_I . The next index denotes the extinction value of the control zone of the respective sheet.

EFFECTS OF IRRADIATION ON PHYSICAL PROPERTIES

The physical properties of a rubber sheet during exposure are closely related to the form of the reaction curves. During exposure in air, the properties of the surface of the sheet do not change at first. At the end of the initial, slowly ascending segment of the reaction curve, however, a rapid increase of the CO groups commences, and the specimen begins to grow sticky. The stickiness then increases rapidly until the steep ascent of the reaction curve again begins to diminish. At the point where the reaction curve becomes flat, stickiness disappears, the surface of the sheet becomes hard, and lacquer-like and, after further exposure, insoluble in benzene. In extracted specimens, an increase of stickiness is observed, which disappears after further exposure, and the surface becomes slightly cracked. On the other hand, if certain active substances are added to rubber, no stickiness is observed. In oxygen, the specimen is sticky during half of the rapid ascent of the reaction curve. In ozone, rubber becomes

quite fluid during exposure. The stickiness depends on the temperature at which the rubber is exposed. It increases with an increase of temperature.

Blake and Bruce²⁵ studied stickiness as a function of the absorption of oxygen, and established that stickiness increases with the duration of exposure, although in many cases it decreases after reaching a maximum. This agrees well with our observations. Houwink²⁴ in his important study of the oxidation of rubber and its colloid-chemical effects, suggested that the appearance of stickiness is a consequence of the molecular disintegration of rubber, which in turn is related to the existence of molecular dipoles. He cites the results obtained by Kohman, who studied the absorption of oxygen by vulcanized rubber in its relation to the appearance of stickiness. We confirmed his results, although the results with unvulcanized rubber are somewhat different. With the absorption of 0.02–0.05 molecules of oxygen (O_2) per $C_{10}H_{16}$ group (that is, with 0.5–1.25 gram-per cent of absorbed oxygen), rubber becomes sticky. With the absorption of 0.5 molecule of O_2 per $C_{10}H_{16}$ group (12 per cent O_2), the stickiness disappears. With the absorption of 1.0 oxygen molecule (24 per cent O_2) per $C_{10}H_{16}$ group, rubber becomes brittle. Accordingly, the rubber is soft at the beginning of oxidation, indicating initial disintegration, then the rubber becomes harder, and finally lacquer-like.

As we observed, these changes are independent of the absolute increase of the $C=O$ groups, but they are related to the experimental conditions and the shape of the reaction curve. For example, rubber samples with the same content of $C=O$ groups (at equal extinction values) in one case may be still sticky, and in another case not sticky, e.g., in an atmosphere of nitrogen, because of the addition of certain agents, when not extracted, etc. Thus, stickiness depends on the mechanism of oxidation, as well as on the absolute quantity of oxygen absorbed; that is, it depends on the degree that the absorbed oxygen causes exclusively destructive reactions and other similar reactions which may progress at the same time. Consequently, the total absorbed oxygen is divided into various types of oxidation products, and this explains the observation of Blake and Bruce²⁵. In general, however, it can be concluded that if the increase of the $C=O$ zone in the rubber spectrum is large (indicated by the increase of the extinction value ΔE at about 0.140–0.200), stickiness will always be observed. In the most highly purified, i.e., longest extracted, rubber samples stickiness appears at $\Delta E = 0.040$.

Asano² and Garner²⁶ exposed rubber in an inert atmosphere or in a vacuum, and observed that the rubber became insoluble, without any appearance of stickiness after exposure. Such rubber behaves as if it were weakly vulcanized. However, it is not so resistant to surface oxidation in air. The longer the product is exposed to light, the less soluble it becomes and the more resistant to the influence of oxygen. Farmer²⁶ and other authors²⁷ ascribe this resistance to organic solvents to the high degree of side-chain formation, which is facilitated by the proximity of the individual molecules in the solid state. Farmer concludes that, if the amount of oxygen absorbed is very small, the molecular weight may decrease considerably, and a relatively slight degree of side-chain formation is enough to cause resistance to solvents. The number of cross-links between the adjacent macromolecules is an index of the good qualities of vulcanizates, even when this number is not great.

From this it is possible to assume, as will be discussed in detail in the explanation of the reaction mechanism, that, in the phase of oxidation where the curves begin to deflect and level off, while the surface of the specimen becomes insoluble, a large degree of side-chain formation takes place. It is true that

this type of vulcanization, which is characterized by a notable decrease of molecular weight caused by rupture of the polymers at the beginning of oxidation, never gives products with the toughness and other good qualities of ordinary vulcanizates, in the manufacture of which oxidation is inhibited as much as possible. The surface of the rubber during this type of vulcanization, which is accompanied at the same time by oxidation, is lacquer-like, insoluble, unelastic, and brittle. However, these properties depend also to a large degree on the experimental conditions and on the nature of the compounding ingredients. During very intense irradiation in air (2.5 cm. at low temperatures), stickiness either is not observed or is only appreciable for a short period, and the final product is relatively elastic and smooth after 2800 minutes' exposure.

RELATION OF THE OXIDATION PROCESS TO THE THICKNESS OF THE SHEET

If sheets of rubber are oxidized to the same degree throughout their thickness, the increase of the $C=O$ groups in a given period is proportional to the thickness of the sheet. The relation between the extinction of the $C=O$ zone

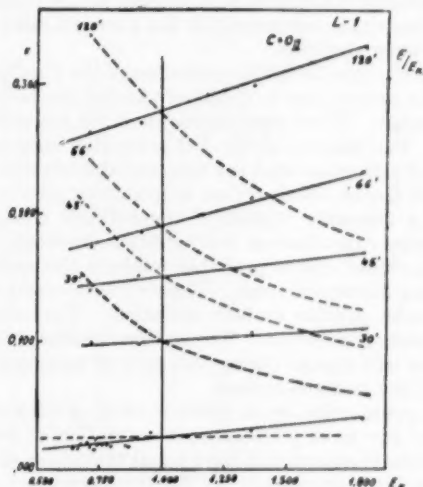


Fig. 11. — Pale crepe irradiated 18 cm. at 28° C (E). — Pale crepe irradiated 18 cm. at 26° C (E/E_K).

E_{CO} (proportional to the number of $C=O$ groups) and the extinction of the control zone (proportional to the thickness of the sheet) should then be constant. As the measurements indicate, this is not so. The relation E_{CO}/E_K for various sheets exposed for the same time is not constant but decreases with increase of thickness. This indicates that oxidation is the more intense, the nearer to the surface is the oxidized layer. Aging by light is thus evidently a surface effect (Figure 11). All the measurements of the photocatalytic aging of rubber are based on absorption methods, so that with thick test-specimens, only a mean oxidation value which does not indicate the very intensive oxidation process on the surface of the rubber is measured.

A method for obtaining perfectly reproducible, extremely thin films has been developed, whereby it is possible to study the oxidation process in films of different thickness by means of infrared spectra. For this reason, infrared spectrography is a very valuable method for investigating the surface resistance of high polymers, such as the effectiveness of photons of varying size, and the decrease of their effectiveness at various depths beneath the surface.

The question then arises whether the more intense oxidation at the surface is not caused by the different concentration of oxygen or ozone which is diffused in the rubber. During exposure to a mercury tube, the concentration of ozone is very small, because ozone is formed by radiation at wave lengths of 1200 to 1800 Å, while it decomposes in the range²⁸ of 3000–3300 Å.

Kuzminskii, Shanin, and Lezhnev²⁹ studied the relation between the concentration of absorbed oxygen and the depth in a specimen 1 cm. thick. According to their measurements, the decrease of concentration of diffused oxygen 0.5 cm. below the surface is 40–60 per cent, and the concentration is practically unchanged directly below the surface (at a depth of 0.01–0.03 cm.). The surface character of oxidation can thus be ascribed to the large absorption of active photons in the thin layers. It is impossible, however, to exclude a certain influence of the increased concentration of oxygen at the surface, since, as will be shown below, the oxygen concentration has a considerable influence on the course of the experimental curves.

Figure 11 shows the relation of the extinction of the C=O zone (5.80μ) to the extinction of the control zone in sheets of varying thickness exposed for 30, 45, 66, and 120 minutes. The dotted curves show the calculated values of the relation E_{CO}/E_K . The relation of the CO extinction zone of the unexposed sheets to the control extinction zone is linear, and the relation is thus constant.

Irregular surface cracks, which appear in specimens of extracted rubber, are probably caused by extensive rupture of the polymer chains resulting from oxidation. Moderate vulcanization can facilitate cracking, since the spatial linking between shortened chains probably weakens the secondary forces between the individual macromolecules. These surface cracks expose the inner layers and thus make possible surface oxidation. The cracks increase and aging progresses deeper and deeper. We can thus conclude that the rheological properties of rubber will change during this type of oxidation in the direction from the surface of the material inward.

The different types of oxidation in sheets of varying thickness make it possible to compare the curves of photocatalytic oxidation of rubber only if the sheets are of the same thickness and have equal extinction of the control zone or if corrections are made graphically for the thickness.

These corrections can be made as follows. The curves of the extinction $E_{C=O}$ as a function of the extinction of the control zone E_K for an equal time of irradiation are constructed (Figure 11). The theoretical equation of the reaction curve for a sheet with equal control zone extinction is easily derived from these curves if the sheet is measured. In fact, all the measurements must be made under identical experimental conditions (intensity of light and temperature). Since, in our measurements, we used different tubes (L1, L2, L3 . . .), we have noted the light source by a special mark in the diagrams. Evidently for each tube, a special correction curve must be constructed.

The surface nature of light aging was also shown by another means. A strongly irradiated (100 minutes, 14 cm.) cube of rubber with a small relative surface area was dissolved in benzene, and films were prepared from this solution. In their spectra, only a negligible increase of the C=O zone was ob-

served, indicating that only a small part of the specimen close to the surface was oxidized.

The increase of $\text{C}=\text{O}$ and $\text{O}-\text{H}$ groups in natural rubber after accelerated oxidation at 125°C is much larger than after photocatalytic aging. This appears in the work of D'Or and Kössler³², as well as from our measurements of films of equal thickness after light aging. This phenomenon also explains the surface nature of light aging. The degree of oxidation decreases with the depth beneath the surface, whereas, in a uniformly heated specimen, the film is

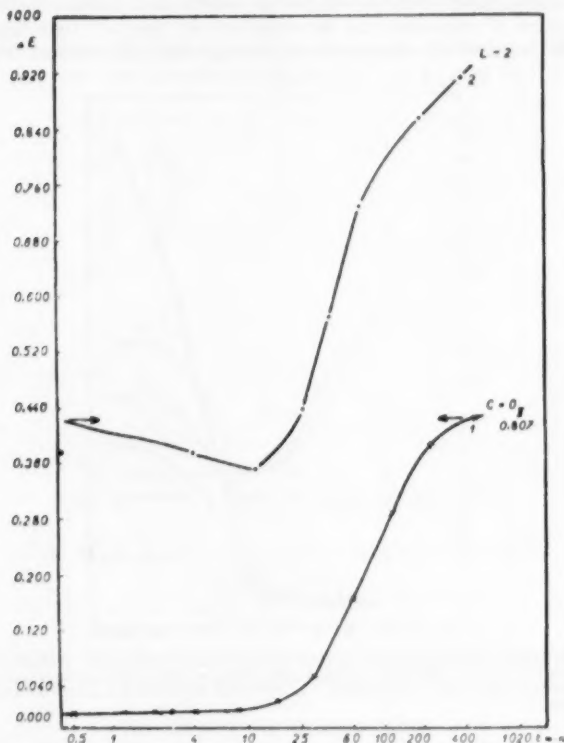


Fig. 12.—1. Pale crepe extracted 432 hours with a mixture of acetone-methanol; irradiated at 14 cm. at 30°C . 2. Pale crepe after 475 minutes' exposure and heating at 125°C .

oxidized throughout at the same time, since oxygen is present in the whole layer in sufficient concentration.

The reaction curves reach maximum points after long exposure. The following experiment was made in order to determine the cause of this phenomenon.

Two specimens of extracted rubber were exposed until the experimental curves leveled off (785 and 475 minutes) and were then heated in a thermostat at 125°C . After the induction period, a rapid increase of $\text{C}=\text{O}$ and $\text{O}-\text{H}$ groups began (Figure 12). This shows that oxidation can progress further by heating, although the curve leveled off after light aging. The time necessary

for chains the initiation of the rapid increase, however, is shorter, because the molecular chains are already partially developed. It is shortened from about 300 minutes to about 30 minutes. This problem will be discussed later.

INFLUENCE OF NITROGEN AND OXYGEN

Rubber films were exposed at a distance of 11 cm. in a quartz cuvette. Filtered air, pure nitrogen, and pure oxygen were run through the cuvette. The experimental curves are shown in Figure 13. In the same period (230 minutes), considerably fewer C=O groups appear in the nitrogen atmosphere. The low degree of oxidation can be explained by the fact that the specimen could not be freed of all oxygen, since the experimental method required fre-

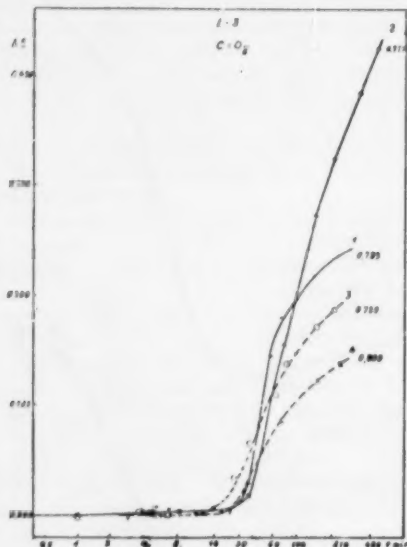


Fig. 13.—1. Pale crepe irradiated in a quartz cuvette at 11 cm. at 28° C in air. 2. Pale crepe irradiated in a quartz cuvette at 11 cm. at 28° C in oxygen; 3. Pale crepe extracted 700 hours with acetone, irradiated in a quartz cuvette 11 cm. at 28° C in nitrogen. 4. Pale crepe irradiated in a quartz cuvette at 11 cm. at 28° C in nitrogen.

quent opening of the cuvette during the measurements. It is thus impossible that only side chain formation (vulcanization) took place, although the specimen did not become sticky during exposure, and until the end of exposure (230 minutes), it remained relatively elastic and smooth. Likewise, no stickiness appeared during exposure of a specimen which had been extracted for 700 hours with acetone, although the reaction was more rapid than in the case of an unextracted specimen in air. The specimen in air became sticky in the time interval of 50–100 minutes, as did the specimen in oxygen. After 150 minutes, however, the stickiness disappeared in the specimen in oxygen, and, at the end of the exposure, all the specimens were lacquer-like.

The concentration of oxygen evidently influences considerably the course of photocatalytic oxidation. We must also consider the possibility of a higher

ozone concentration, although an atmosphere of ozone causes liquefaction rather than the formation of a lacquer-like surface.

As is seen from the curves and the physical characteristics of the specimens, the more favorable are the conditions of vulcanization, i.e., low temperature, vulcanization by ultraviolet radiation in nitrogen, the lower are the curves after the final leveling off.

Blake and Bruce²⁵ showed that the degree of oxidation is not proportional to the partial pressure of oxygen. According to works of Williams and Neal⁴⁰ and Morgan and Naunton⁴¹, oxidation is independent of the oxygen pressure if the size of the specimen is such that the oxygen can be diffused through it with sufficient rapidity.

Although, in our experiments, the exact relation of oxidation to the concentration of oxygen was not established, it is safe to assume that the increase

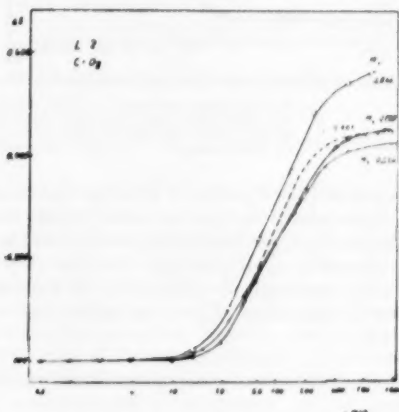


Fig. 14.—Pale crepe extracted with acetone, irradiated at 14 cm. at 30° C.

A₁ 648 hours' extraction
A₂ 432 hours' extraction
A₃ 216 hours' extraction

of the C=O groups and the related increase of the O—H groups depends on the oxygen concentration in contact with the rubber during exposure.

INFLUENCE OF EXTRACTION

Crude rubber shows relatively good resistance to aging before it is processed technically. As is known, the reason for this is the presence of natural anti-oxidants. It is seen from the form of the curves that these substances are effective not only against heat aging²³ but also against photocatalytic aging.

Specimens of pale crepe were extracted for various periods (215, 432, and 648 hours) with acetone, methanol, and a mixture of the two (in the proportion of 1:1). One gram of rubber was extracted in 100 cc. of liquid, which was changed every 72 hours. The curves for these specimens are shown in Figures 14, 15, and 16.

Acetone and methanol have different effects. Acetone, as is seen, greatly shortens the initial, gradually ascending part of the curves, and the curves level

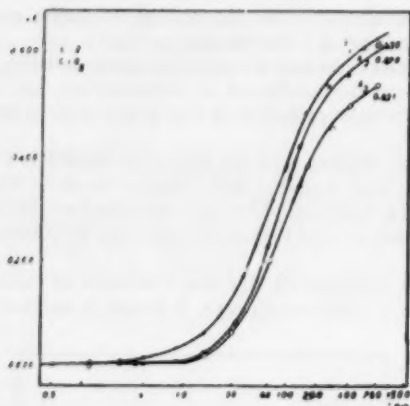


Fig. 15.—Pale crepe extracted with methanol, irradiated at 14 cm. at 30° C.

M₁: 648 hours' extraction
 M₂: 432 hours' extraction
 M₃: 216 hours' extraction
 C: Unextracted

off later. The increase of C=O groups is greater, the longer the time of extraction, that is, the more nearly the natural antioxidants are eliminated. The curve may level off earlier during extraction with methanol as in the unextracted specimen, while the degree of oxidation may decrease (top of the curve). In general, extraction with methanol, in distinction to extraction with acetone, has only a slight effect on the initial stage of oxidation, and only after very long extractions (Figure 15).

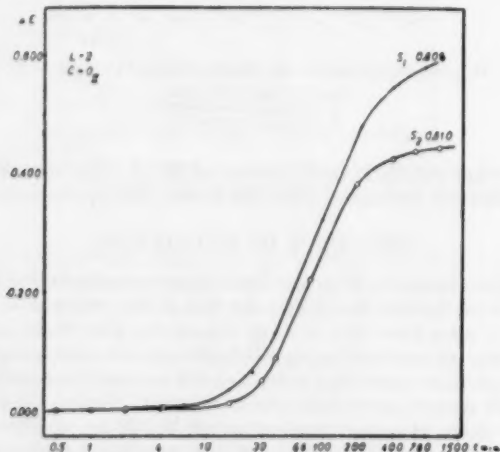


Fig. 16.—Pale crepe extracted with 1:1 acetone-methanol mixture, irradiated at 14 cm. at 30° C.

S₁: Extracted 648 hours
 S₂: Extracted 432 hours

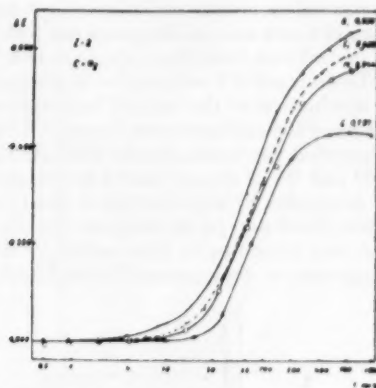


FIG. 17.—Pale crepe irradiated in air at 14 cm. at 30° C.

C Unextracted

A₁ Extracted 648 hours with acetoneM₁ Extracted 648 hours with methanolS₁ Extracted 648 hours with 1:1 mixture of acetone and methanol

This indicates that, in natural rubber, in addition to natural antioxidants, natural catalysts of photooxidation also are present. Acetone eliminates chiefly the antioxidants, while methanol also eliminates the oxidation catalysts. The effect of a mixture is additive (Figures 16, 17, 18). Further experiments, in which about 0.4 per cent tyrosine (by weight) was mixed into the rubber, indicate the presence of natural catalysts of oxidation in natural rubber. Tristram⁴² determined the presence of tyrosine, besides other aminoacids, in the analysis of proteins from the latex of *Hevea brasiliensis*. In these experiments, oxidation was increased, as will be noted later in the study of oxidation catalysts.

Thus, natural oxidation-reduction systems, i.e., antioxidants and oxidation catalysts, are present in natural rubber, and the nature of these determines the resistance of rubber to aging.

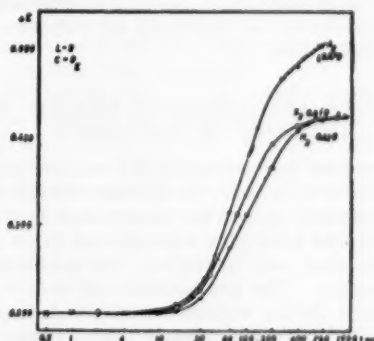


FIG. 18.—Pale crepe extracted 432 hours.

A₂ With acetoneM₂ With methanolS₂ With 1:1 acetone-methanol mixture

In the spectra of unexposed specimens which have been extracted for a long time, almost all the original C=O and O—H groups are lost. The specimens, however, must be kept in darkness in an inert atmosphere after the extracting liquid is eliminated. The decrease of C=O and O—H groups during extraction indicates not only the elimination of the natural oxidation-reduction system, but also partial elimination of the oxidized short chains. This is also confirmed by experiments with extracted specimens slowly oxidized in air, which again show a decrease of C=O and O—H groups after a second extraction.

This observation is confirmed by experiments of Kemp and Peters⁴⁹, who determined the proportion of sol and gel in solutions of crude rubber and products of oxidized crude rubber, according to their solubility in petroleum ether. On the basis of these experiments, they assume that sol rubber is an oxidation

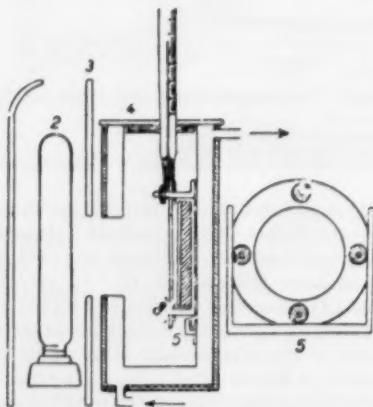


FIG. 10. 1. Clay shield. 2. Mercury quartz tube. 3. Asbestos. 4. Brass jacket and cover with insulating cork layer, thermometer, water inlet and outlet, and ultrathermostat. 5. Brass frame with small plate covered with the rubber film, which slides into the cavity.

product of gel rubber whose composition is probably represented by $(C_4H_8)_nO_2$. This explanation, however, can be valid only for polymers in which no side-chain formation has taken place.

RELATION OF THE OXIDATION PROCESS TO THE INTENSITY OF RADIATION

Three methods were used in determining the relation between the oxidation process and the intensity of radiation. In one case, the specimens were exposed in a quartz cuvette in filtered air, and the temperature in the cuvette was kept at 27° C; in the second, the specimens were exposed in air while the temperature was gradually increased; and in the last, the specimens were exposed in air at constant temperature. The temperature was carefully controlled during the measurements, since, during exposure at short distances (2–5 cm.), the temperature rose to 60° C and, consequently the curve showed certain irregularities in the later stages, descending considerably after reaching a maximum. A rubber film on a sodium chloride plate in a sliding frame was exposed in a metal case with a double jacket in which water was circulated, and was kept at

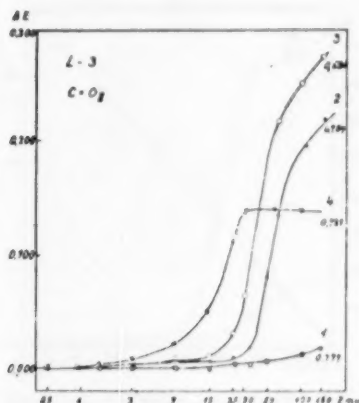


FIG. 20.—Pale crepe irradiated in quartz cuvette at 28° C.

1. At 25 cm.
2. At 11 cm.
3. At 6 cm.
4. At 3.5 cm.

constant temperature by a thermostat. The case was provided with a thermometer, and had an observation window close to the source (2.5 cm., see Figure 19).

The curves of increase of C=O groups during exposure in a quartz cuvette are shown in Figure 20. The distance of the source from the film was 3.5, 6, 11, and 25 cm. The relation between the distance from the source and the time, in minutes, in which the increase of extinction $\Delta E_{C=O} = 0.020$, that is, the approximate value at which the curves begin to ascend rapidly is at first linear (Figure 21). Likewise, if the relation between $1/r^2$ where r is the distance from the source, and the increase of $\Delta E_{C=O}$ for 30 minutes' exposure is plotted on a graph, a straight line is obtained (Figure 22). Since $\Delta E = k \cdot 1/r^2 = k' \cdot J$ where J is the intensity of the light, we may conclude that the rate of photocatalytic oxidation at constant temperature is proportional to the intensity of the radiation. The relations are more complicated if the temperature of the specimens rises at the same time (Figure 23).

The change of the curves with an increase of temperature may explain the higher degree of vulcanization with the same concentration of oxygen. Oxidation thus proceeds much faster at first. However, the points susceptible to

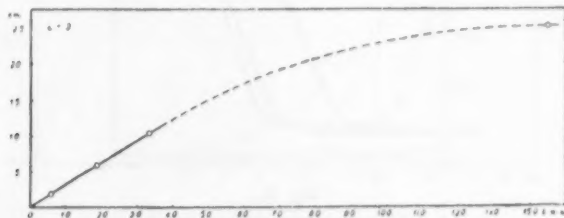


FIG. 21.— $\Delta E_{C=O} = 0.020$ during irradiation in quartz cuvette.

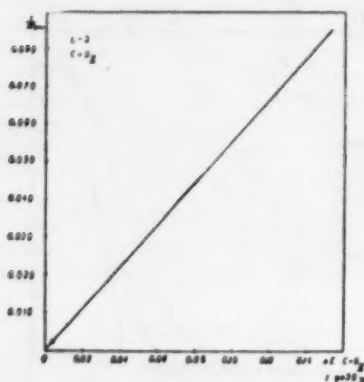


Fig. 22.—Pale crepe irradiated in quartz cuvette.

oxidation are quickly exhausted by side-chain formation, e.g., direct and without oxygen taking part or by rapid rupture of hydroperoxide groups. If however, the temperature is considerably lower (14°C), a notable decrease of oxidation appears; this is evident in the lengthening of the induction period, as well as in the fall of the curve (Figure 24).

The initial, gradually ascending part of the curves is somewhat shorter for thin films than for thick ones. This is due to the surface nature of oxidation, because the absorption of photons is more intense on the surface layer and their effect decreases with thickness. The more photons are absorbed, the more free radicals are formed, and these latter initiate oxidation, for example: $\text{RH} + h\nu \rightarrow \text{R}\cdot + \text{H}\cdot$, RH .

Oxidation is accelerated with time, and this indicates that photocatalytic aging is a chain process. The induction period of such a process depends on the number of free radicals formed. The more intense the irradiation, the more free radicals are formed, and the shorter is the initial, gradually ascending part of the curves. This part of the curves thus furnishes relative data on the rate of initiation or tendency to form free active radicals.

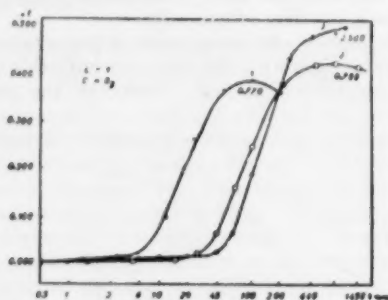


Fig. 23.

1. Pale crepe irradiated at 3.5 cm. at 55°C
2. Pale crepe irradiated at 14 cm. at 30°C
3. Pale crepe irradiated at 18 cm. at 27°C

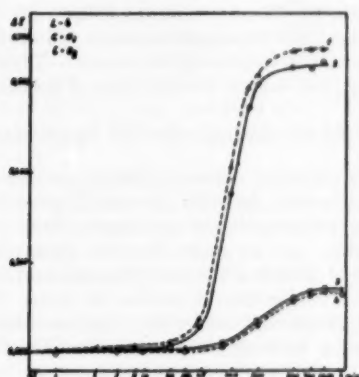


Fig. 24.—Pale crepe irradiated in a thermostat at 2.5 cm.

1. C=O_I at 62° C
2. C=O_{II} at 62° C
3. C=O_{III} at 14° C

Our experiments show that the relations are very complex with respect to the combined influence of light and heat, and their study can give valuable information about the reaction mechanism. This problem will be discussed further in a later work.

In the study of oxidation as a function of the time of exposure, specimens of pale crepe were exposed for equal periods, which were shorter than the time necessary for a rapid ascent of the curves (2.5 minutes). The curves were absolutely identical to those obtained in the usual way, i.e., by exposure after

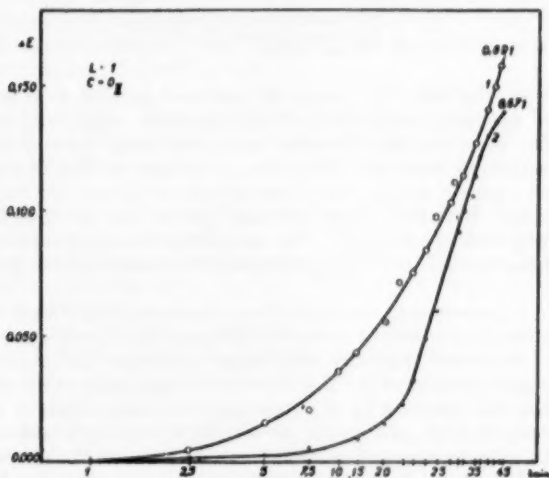


Fig. 25.

1. Extracted pale crepe, irradiated at 18 cm. at 28° C
2. Unextracted pale crepe, irradiated at 18 cm. at 28° C

double intervals; 2, 4, 8, 16, 32 . . . minutes (Figure 25). It is seen that the reaction after an interval and repeated exposure follows the same course, regardless of the length of the individual exposures. Thus it depends only on the number of photons, and not on the duration of their action.

INITIATION OF OXIDATION BY FREE RADICALS

When pale crepe containing 5 per cent benzoyl peroxide is irradiated, oxidation takes place so rapidly that the initial, gradually ascending part of the curve is not observed; the curve rises steeply and linearly from the beginning. Rubber ages rapidly in light. As we know, benzoyl peroxide tends to form free radicals ($R-CO-O-O\cdot$) after absorbing photons, and these radicals shorten the induction period of oxidation of rubber in light. The peroxide bond, $-O-O-$, is relatively weak and can be decomposed chemically, or it becomes a catalyst of oxidation by forming $H-O\cdot$ and $R-CO-O\cdot$ radicals⁴⁴.

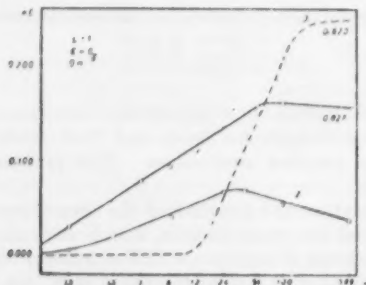


Fig. 26.—Pale crepe irradiated at 18 cm. at 28° C.

1. 5% Benzoyl peroxide, C=O
2. 5% Benzoyl peroxide, O-H
3. Without peroxide

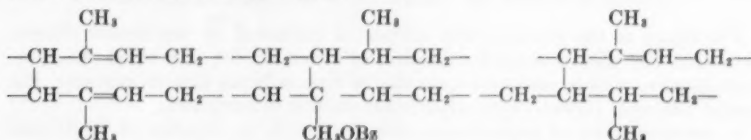
In Figure 26, the fall of the curve (in the level part) is most evident and most notable compared with that of the specimen containing no benzoyl peroxide. The more rapidly oxidation progresses from the beginning of exposure, the greater is this fall. The effect is similar to that of very intense radiation from a nearby source, when free radicals are formed for the most part photochemically. It appears that the initial period and the final level phase are governed by different factors. This means that it is impossible to predict the height of the curve in the level phase from the length of time of the induction period.

Here, too, a phenomenon similar to that observed in specimens exposed to intense radiation from a nearby source is observed; the C=O groups, like the O-H groups, decreased gradually after longer exposure. D'Or and Kössler³³ observed a similar decrease of O-H groups in the heat aging of rubber. These authors explain this decrease by the subsequent decomposition of the hydroperoxide groups, while no new groups are formed because of a lack of points of initiation. In measurements at medium intensities and in the absence of substances which release free radicals, no such decrease is observed. This is understandable in view of the surface nature of photocatalytic oxidation. The experimental curves ascend slowly and level off after longer exposure, because

oxidation can gradually penetrate inside. If, under special conditions, e.g., with an inhibitor present or in a nitrogen atmosphere, a stable uncracked surface film is formed, and this can survive increasing oxidation and may completely inhibit any further formation of oxidation products. It is possible that the decrease of C=O and H—O groups observed after very long exposure (280 minutes) indicates a change of these groups into higher oxidized forms as a result of further oxidation.

The lowering of the level part of the curve in the presence of benzoyl peroxide is explained by the fact that vulcanization, caused by the large quantity of free radicals, takes place at the same time as oxidation, while the side-chain formation exhausts the points susceptible to oxidation. Accordingly, specimens containing peroxide are hard, smooth, and uncracked after 60 minutes' exposure.

Benzoyl peroxide⁴⁶ reacts very readily with rubber at 140° C. It is also known that benzoyl peroxide breaks down into free radicals above 100° C, and these can recombine and initiate chain reactions in olefins⁴⁶. The most significant result of the different reactivity of these radicals is the capacity to form cross-links between olefin and aromatic molecules, with or without direct linking of the phenyl or benzoyl groups to the side products. Farmer⁴⁷ describes these types of such vulcanization.



The best concentration of vulcanizing agent in the heat reaction is 10 per cent benzoyl peroxide by weight of the rubber⁴⁸, while one-third of this quantity will react directly with the rubber. The lowest temperature for good vulcanization is 80° C. According to Stevens⁴⁹, heat and light increase the rubber-peroxide reaction, and the photochemical effect is stronger. If any of the three types of side-chain formation takes place during exposure, it will be at the expense of an increase of C=O groups.

If the peroxide content is small, the specimen will not become insoluble, but will become sticky. Blake and Bruce⁵⁰ added 2 per cent of benzoyl peroxide to rubber and observed the oxygen absorption. The test specimens became very sticky after a short time, evidently because of their high degree of oxidation.

Thus the influence of benzoyl peroxide on vulcanization, or on oxidation, depends on the experimental conditions. In the experimental curves, oxidation is indicated by the immediate rapid increase of the C=O groups, while the slow increase of $\Delta E_{\text{C=O}}$ denotes vulcanization. This is reflected in the lowering of the flat part of the curve.

If rubber which has been masticated for 32 minutes with 5 per cent of benzoyl peroxide is irradiated, the increase of oxidation will be much more rapid and the flat part of the curves much higher than those for pure unmasticated rubber containing no benzoyl peroxide. The disagreement between our results and the measurements of Blake and Bruce, who observed a much greater absorption of oxygen, can easily be explained by the fact that, during mastication, rubber becomes much more susceptible to photocatalytic oxidation, especially in the presence of benzoyl peroxide. As will be discussed later, this susceptibility is indicated by the increase of $\Delta E_{\text{C=O}}$ of about 2 per cent after

2 minutes' mastication, even without peroxide, and about 50 per cent after 32 minutes. The lowering of the level part of the curves of samples containing peroxide in comparison with samples without peroxide suggests that, although oxidation is very rapid at first and begins even before irradiation, the entire process (represented by the increase of $C=O$) can not reach a much higher degree. Since Blake and Bruce prepared their test-specimens by compressing rubber which had been previously masticated for a short time, the specimens became more susceptible to photochemical oxidation, i.e., to great absorption of oxygen.

EFFECT OF NEGATIVE CATALYSTS OF OXIDATION (INHIBITORS AND RETARDERS)

In the study of the effectiveness of various negative catalysts of photochemical oxidation, very diverse curves were obtained. These negative catalysts, representing various types of organic substances, either only delay oxidation (retarders) or reduce it at the same time (inhibitors). Since numerous measurements were made, their results will be published in a special article.

CONTINUATION OF OXIDATION AFTER EXPOSURE

The shape of the experimental curves, as indicated by the results shown, shows that the photocatalytic oxidation of crude rubber is a chain reaction. Consequently, with a sufficient quantity of free radicals (active centers), the reaction proceeds further, even after irradiation is interrupted.

In another series of experiments, the change of the number of $C=O$ and $O-H$ groups formed after an exposed specimen was kept in a desiccator in darkness for a given period, was measured. When the specimens were exposed for only a short time, i.e., shorter than the induction period, no structural changes in darkness were observed. This is explained quite simply by the absence of free radicals, which are necessary for the development of a chain reaction.

When the specimens were exposed for a period exceeding the induction period, i.e., until the curves began to ascend rapidly, the following changes were observed.

In unextracted pale crepe, the number of $C=O_I$ and $C=O_{II}$ groups was practically unchanged.

In pale crepe extracted with acetone, $E_{C=O_I}$ (at low frequency) increased slowly, while $E_{C=O_{II}}$ (at high frequency) decreased slowly. This phenomenon can be explained by partial association of the $C=O$ groups by means of hydrogen bridges, most of which had been ruptured because of the absorbed energy.

The $C=O$ doublet appears in the spectrum of more highly oxidized samples. Here the decrease of $E_{C=O}$ at high frequencies and the increase at low frequencies can be explained by the slight shift of the whole zone toward the lower frequencies. The causes were cited above. This change, however, was observed only in extracted rubber, where the natural oxidation-reduction system was partially eliminated. When these oxidation-reduction systems are present in rubber, the shift toward the lower frequencies is not observed in darkness. The increase of $C=O$ and $O-H$ groups in long-extracted rubbers was particularly rapid when the latter were exposed for about 30 minutes (until the beginning of the ascending part of the curve; L-1).

The $O-H$ groups in unextracted as well as in extracted rubber increase in darkness (for example, in an extracted rubber sample, $\Delta E = 0.072$, in an unex-

tracted sample, $\Delta E = 0.041$). After shorter irradiation, this increase appears only when benzoyl peroxide is added to the rubber. This confirms the conclusion that oxidation is governed primarily by the O—H groups (probably hydroperoxides) and the rate of their formation is governed by the free radicals (see Figure 27).

The number of double bonds is practically constant. A decrease of the C=O_I and C=O_{II} zones was also observed after longer exposure; for example, after exposure for 876 minutes and after a week in darkness, $\Delta E_{C=O_I} = -0.025$ and $\Delta E_{C=O_{II}} = -0.045$). This indicates that oxidation takes place even in darkness in specimens exposed for a long time, and proceeds from the C=O groups to other groups. Benzoyl peroxide accelerates this decrease of C=O groups.

The addition of benzoyl peroxide causes a slight increase of the number of O—H and C=O groups, even without intense irradiation of the rubber.

If effective antioxidants are added to rubber, no changes are observed in the spectrum in darkness, even after several days.

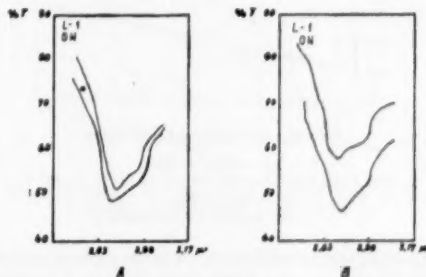


FIG. 27.—A. 1. Pale crepe irradiated 876 minutes at 18 cm. at 28° C. 2. Pale crepe irradiated 876 minutes at 18 cm. at 28° C after one week in darkness. B. 1. Pale crepe extracted with acetone, irradiated 876 minutes at 18 cm. at 28° C. 2. Pale crepe extracted with acetone, irradiated 876 minutes at 18 cm. at 28° C, after one week in darkness.

The changes in darkness after the formation of a sufficient number of free radicals by irradiation of rubber confirm the assumption of a chain reaction of catalytic aging by light.

RELATION OF PHOTOCATALYTIC AGING TO MASTICATION

During mastication, the polymeric molecules of rubber are shortened, with ensuing structural changes, as will be described later. The following measurements show the degree to which the photocatalytic aging of rubber depends on these changes.

Films were prepared from specimens of pale crepe which had been masticated for 2, 8, 32, and 50 minutes. These specimens were exposed for 60 minutes under normal experimental conditions. Since the films were not all equally thick, the increase of $\Delta E_{C=O}$ of specimens masticated for various periods was compared with Figure 11. The extinction value for an unmasticated specimen exposed 60 minutes E_{CO}^n was determined for the extinction control zone like that of a film prepared from masticated rubber. This value was subtracted from E_{CO}^t of a masticated specimen exposed 60 minutes. The difference, $E_o - E_{CO}^n$, gives the increase, ΔE_{CO} , caused by masticating crude rubber for a

specimen exposed 60 minutes. The differences in the increase of oxidation of specimens masticated for various periods and unmasticated specimens are shown in the graph in Figure 28. As will be explained in later work, the C=O groups increase as a result of mastication. The lower curve in Figure 28 represents the increase of ΔE of these groups as a result of mastication (unexposed specimen). The values of ΔE are here again the difference between the extinction E_{CO}^* of a masticated specimen and E_{CO}^* of an unmasticated specimen of equal thickness (in the same control zone). This curve is identical with that

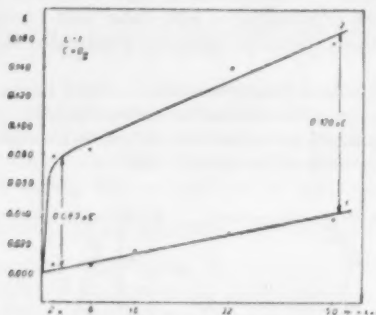


FIG. 28.—1. Unexposed pale crepe

$$\Delta E = E_{CO}^* - E_{CO}^*$$

2. Pale crepe irradiated 60 minutes at 18 cm. at 28° C.

$$\Delta E = E_{CO}^* - E_{CO}^*$$

$\Delta E'$ increase by mastication.

of the increase of C=O groups with time of mastication, constructed by separating the extinction of the control zone, described in a previous work². Both methods give similar results, and thus confirm the accuracy of the correction. The differences between the two curves, for an exposed and an unexposed specimen, are a measure of the increase of susceptibility of rubber to photocatalytic aging as a result of mastication.

As we see, at the beginning of mastication (about 2 minutes), this susceptibility increases rapidly; after this, however, it increases slowly and uniformly

TABLE 2

Time of mastication	$\Delta E = E_{OH}^* - E_{OH}^*$ Exposed 60 min.	
	E_{OH} wave length	$E_{OH\text{Assoc.}}$
2	0.092	0.035
8	0.094	0.054
32	0.143	0.089
50	0.117	0.071

with the time of mastication. This high susceptibility is due in part to the increase of double bonds, which was observed spectroscopically, and in part to the decrease of viscosity, as a result of which the mobility of the free radicals may increase. The change of the number of O—H groups in specimens masticated for various periods was studied after exposure for 60 minutes. The results are shown in Table 2.

The longer that rubber is masticated, the greater the number of OH groups formed during subsequent exposure. After mastication for 50 minutes, how-

ever, the OH groups decrease, probably reacting with CO, as was observed in samples containing benzoyl peroxide and exposed at short distances from the source of radiation.

In the analysis of the structural changes caused by mastication, as will be shown in a later work, the hydroxyl groups increase slightly in the range of free O—H groups, at 2.96μ . During exposure, however, they are formed in the range of unassociated O—H groups at 2.86μ . When masticated rubber is irradiated, O—H groups appear in the high-frequency range, in addition to O—H groups in the low-frequency range. Consequently, broad absorption is observed in the spectrum (Figure 29).

The milled samples become sticky and greasy during mastication, and the stickiness of the films increases on exposure to radiation. If a sample is masticated for 32 minutes with 5 per cent benzoyl peroxide, and is then irradiated, oxidation becomes more rapid. If sticky samples masticated for a long time

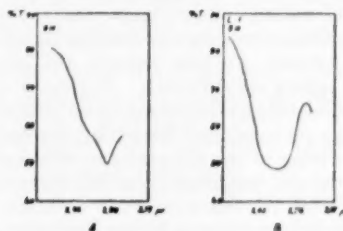


Fig. 29.—A. Pale crepe masticated 50 minutes. B. Pale crepe masticated 50 minutes, irradiated 600 minutes at 18 cm. at 28°C .

are left for a long time in air, after a few months their surface becomes lacquer-like and smooth, even if no light reaches them, while, below the surface, they become greasy and sticky.

SUMMARY

1. The qualitative changes in the infrared spectrum of crude rubber during exposure of films 0.02–0.03 mm. thick to a mercury quartz lamp are described. The shape of the new band which appears after long exposure at 5.66μ indicates the presence of carboxyl groups, as well as aldehyde and ketone groups. This band is centered at 5.80 to 5.82μ . Besides the original hydroxyl groups observed in crude rubber, which are absorbed at 2.98 – 2.96μ , a new intense band appears at 2.86μ during irradiation. In masticated rubber, the band is at 2.96μ , that is, in the range of OH groups associated with hydrogen bridges. It is suggested that the new band represents unassociated OH groups. Both bands are displaced during irradiation toward higher frequencies.

2. The increase of C=O, O—H, and C—H groups, the decrease of CH_2 and CH_3 groups, and isoprene units, and the change of C=C groups were studied quantitatively, as well as the band at 10μ , at which the C—C groups probably vibrate. The experimental curves representing the increase of extinction of the characteristic band as a function of the logarithm of the time is S-shaped. After an initial, slowly ascending period, a rapid ascent is observed, after which the curve again becomes flat or changes only slowly. The changes in the shape of the curves provide valuable information about the mechanism of photochemical oxidation.

3. The physical characteristics of the rubber samples are closely related to the course of the experimental curves. Specimens exposed in air are most sticky in the oxidation phase, which is represented by the rapidly ascending part of the curve. After the curve levels off, stickiness disappears and the specimen becomes hard, lacquer-like, insoluble in benzene, and sometimes cracks. This curve indicates an initial rupture of the polymers at the beginning of oxidation and prevalent side-chain formation after long exposure.

4. The surface character of light aging is shown. A spectrographic method of studying the surface resistance of high polymeric substances to light is described, as well as a study of the effectiveness of photons of varying size which strike the surface of the material, and the decrease of their effectiveness at various depths beneath the surface.

5. The final flat part of the curves is lowered by exposure in an atmosphere of nitrogen, while it is higher for oxygen than for air.

6. The time of extraction of crude rubber also has a similar effect. The higher the proportion of natural antioxidants eliminated, the more rapid is oxidation at the start. This is indicated by the shortening of the initial, slowly ascending part of the curves. In this respect, the effects of acetone and methanol as extraction agents are different. Methanol, in distinction to acetone, also eliminates the natural oxidation catalysts at the beginning of extraction; this may appear in a prolonging of the initial, gradually ascending section of the curves or in a lowering of the flat section. The oxidation process thus depends largely on the natural oxidation-reduction system in the rubber.

7. It is shown that, when the temperature is constant, the initial period of photocatalytic oxidation is proportional to the intensity of radiation. However, during very intense irradiation at low temperatures, the low flat section of the curves, and also the appearance of the surface of the specimens, indicate simultaneous intensive side-chain formation. The increased absorption of photons greatly accelerates the formation of free radicals, which start the chain mechanism of aging. The radical nature of the reaction was confirmed by a study of crude rubber containing benzoyl peroxide. If irradiation or direct addition of substances which provide free radicals causes the formation of a sufficient number of reaction centers, the reaction continues, after exposure is interrupted, for a certain time, even in darkness. This continuation of the reaction is not observed if an effective oxidation inhibitor is added to the rubber.

8. Mastication of natural rubber increases considerably its susceptibility to deterioration on exposure to light. The relation of this increased susceptibility to the time of mastication is shown graphically.

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INHIBITED OXIDATION OF ELASTOMERS *

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The oxidation of elastomers is a fundamental cause of aging. The action of atmospheric oxygen is principally directed at the double bonds of the hydrocarbon chains. The active peroxides formed as a result of this initial reaction, spontaneously decomposing, cause rupture of the molecular chains or, stabilizing, are absorbed by the rubber and are a cause of the side-chain degradation process of autocatalytic oxidation. Besides this rupture of the chains, polymerization and recombination of the radicals also take place. Autocatalysis is a very intensive process, and leads rapidly to complete loss of valuable technical properties in rubber.

In practice, elastomers are almost always protected by antioxidants which inhibit oxidation. Good inhibitors break the reactive chains at the first link, converting oxidation into a non-chain process, that is, reducing it to an initiation reaction. Widely used antioxidants, such as aromatic amines, are such inhibitors.

Any direct study of the kinetics of absorption of oxygen by rubber which contains an inhibitor is a very difficult task, since such a study requires sensitive methods of determining the absorbed oxygen. The work of Koshelev and Ysenkova¹ and other authors² has shown that secondary aromatic amines, e.g., phenyl-2-naphthylamines, are decomposed during the aging of rubber.

STUDY OF OXIDATION OF ELASTOMERS IN THE PRESENCE OF PHENYL-2-NAPHTHYLAMINE

The study of autocatalytic oxidation is, of course, of great theoretical importance. The laws observed during this process are different from those which govern inhibited oxidation. From this it follows that to use data obtained during autocatalysis directly for the solution of practical problems does not have sufficient foundation, and this includes the practical use of raw or vulcanized rubber containing an inhibitor.

The rate of free oxidation, i.e., with no antioxidant present, of hydrocarbons by oxygen is, according to Medvedev³, regarded as consisting of two components: (1) w_1 —the rate of the process resulting from the initial reaction of the oxygen with the original substance (rubber, in this case), and (2) w_2 —the rate of the autoaccelerated process (formation of side chains). The mechanisms of the two processes which govern w_1 and w_2 are different. In the measurable stage of autocatalysis, $w_2 \gg w_1$, while in the presence of a true inhibitor, right up to quite small concentrations of inhibitor, $w_2 = 0$, and w_1 is greatly decreased.

If the rate of initiation is designated by w_i , and the rate of inhibited oxidation by w_{in} , then in the presence of an inhibitor:

$$w_i \leq w_{in} \ll w_1 \quad (1)$$

* Translated from RUBBER CHEMISTRY AND TECHNOLOGY from *Khimia i Fiziko-Khimia Vysokomolekulyarnykh Soedinenii, Doklady 7-oi Konf. Vysokomolekul. Soedineniyam*, 1952, pages 90-98.

The basic form of rupture of the chains here is rupture by the inhibitor. Rupture caused by the absorption of oxygen may have some role.

The probability of rupture is proportional to the concentration of the agent which causes rupture:

$$K_i[i] + K_{O_2}[O_2] = 1 \quad (2)$$

where K_i is the constant of rupture by the inhibitor i , and K_{O_2} is the constant of rupture by oxygen. For a good inhibitor: $K_i \gg K_{O_2}$, nevertheless, in many cases, the value of K_{O_2} can still not be disregarded.

If $K_i[i]_{cr} = 1$, the concentration of inhibitor is critical. Below this concentration, autocatalysis develops in the presence of an inhibitor. If the anti-oxidant is an effective one, then $[i]_{cr}$ is very small.

From what has been said above, it follows that the rate of oxidation w_{ox} is very close to w_i , and, in the case of constant oxygen pressure, it can be considered identical, with only slight possibility of error.

We shall see that the condition: $K_i[i]_{cr} = 1$, is an approximate expression of the greatest probability of rupture, since this probability follows a certain statistical distribution.

The study of the inhibited oxidation of rubber which is not activated by positive catalysts and mechanical stresses is made easier by the fact that the diffusion factor does not play an important part.

We studied the kinetics of inhibited oxidation indirectly by investigating the kinetics of decomposition of phenyl-2-naphthylamine. Oxidation was carried out in an apparatus described by Kuzminskii⁴. Since, during oxidation, rubber gradually combines with an amine, the kinetics of the process can be studied by determining the quantity of free inhibitor which can be extracted by methanol at various stages of oxidation. Because it was necessary to work with thin sheets, the absolute amounts of inhibitor were very small, and could be measured only by sensitive methods of analysis, such, for example, as absorption spectrometry in ultraviolet light or colorimetry by a method of quantitative determination of phenyl-2-naphthylamine especially developed by the authors. This consists of obtaining an azo dye by the combination of phenyl-2-naphthylamine with diazotized p-nitroaniline in methyl alcohol in the presence of an acetate buffer at pH = 5-6. For control purposes, the bound inhibitor was measured on the basis of the quantity of residual nitrogen in the extracted film. To this end, the latter was calcined according to Kjeldahl and the ammonia absorbed in sulfuric acid was measured colorimetrically after addition of a Nessler reactive.

The kinetic curves of consumption and combination of phenyl-2-naphthylamine during the oxidation of sodium-butadiene rubber in the presence of various percentages of inhibitor and during oxidation at various temperatures are shown in Figures 1 and 2. It can be seen from these figures that the kinetics of consumption of the inhibitor is linear, and that the rate of the process (tangent of the angle of inclination of the curves) increases with the temperature. We shall make two suggestions concerning the processes which take place:

- (1) Oxygen (O_2) reacts with a polymer P at the double bond, i.e.;



where n_0 is the initial active center—the radical peroxide.

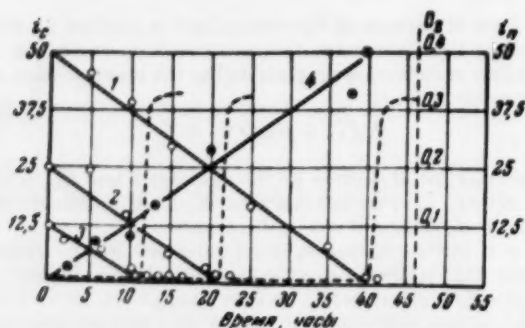


Fig. 1.—Kinetics of consumption and combination of phenyl-2-naphthylamine at various initial concentrations in rubber. Temperature 120° C. Curves 1–3. Consumption of inhibitor and absorption of oxygen; Curve 4. Increase of bound inhibitor; i_c Free inhibitor in millimoles per l. of rubber; i_n Bound inhibitor in millimoles per l. of rubber; O_2 Absorbed oxygen in millimoles per mole of rubber. The abscissa indicates the time in hours.

(2) The reaction of the active center (n_0) with the inhibitor (b) proceeds in the ratio 1:1, i.e.:

$$n_0 + b = x$$

where x is the product of the reaction.

The picture changes little if the inhibitor is bifunctional or polyfunctional and reacts with some of the active centers.

Since the number of double bonds consumed can be disregarded in the inhibition period, and oxygen is present in abundance, then:

$$\frac{dn_0}{dt} = K_1[P][O_2] = \text{const.} = w_1$$

on the other hand:

$$-\frac{dn_0}{dt} = -\frac{db}{dt} = K_2[n_0][b]$$

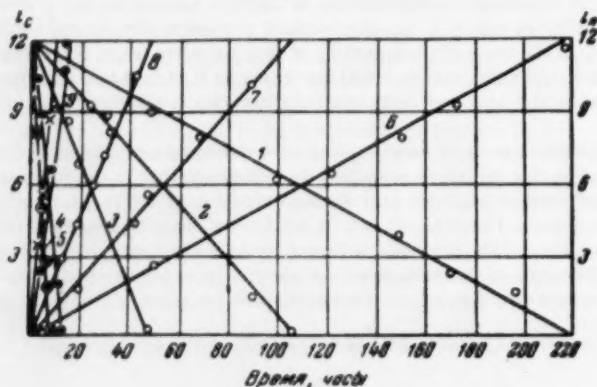


Fig. 2.—Kinetics of consumption (curves 1–5) and combination of phenyl-2-naphthylamine (curves 6–10) during oxidation of sodium-butadiene rubber. Initial concentration of inhibitor 12 millimoles per l. Temperature 90° C (1.6); 100° C (2.7); 110° C (4.9); 130° C (5.10); i_c Free inhibitor in millimoles per l. of rubber. i_n Bound inhibitor in millimoles per l. of rubber. The abscissa indicates the time in hours.

For the stationary period:

$$K_i[P][O_2] = K_n[n_0][b] = w_i = -\frac{db}{dt} \quad (3)$$

Thus the rate of consumption of the inhibitor is equal to the rate of initiation. Knowing $[P]$ and $[O_2]$, one can easily calculate the constant of initiation K_i and, from the data for the change of this value with the temperature, find the activating energy of initiation, the value of the preexponential factor in the Arrhenius' equation, etc.

At sufficiently high temperatures in the absence of any inhibitor, the period of autocatalytic oxidation is very short and cannot be measured directly. In the presence of an inhibitor, this period (the inhibition period in this case) is governed by the amount of phenyl-2-naphthylamine added, as may be seen in Figure 3.



FIG. 3.—Relation between phenyl-2-naphthylamine content in sodium-butadiene rubber and the length of the inhibition period. Temperature 120° C. The ordinate indicates the period of inhibition in hours; the abscissa indicates the concentration of inhibitor, in millimoles per l., in the rubber.

INFLUENCE OF VARIOUS FACTORS ON THE RATE OF INITIATION OF THE OXIDATION OF RUBBER

At every temperature, w_i is a constant for any given type of rubber. The influence of the type of rubber will be considered later. The influence of the partial pressure of oxygen on the rate of consumption of the inhibitor during the oxidation of sodium-butadiene rubber at 120° C is shown in Figure 4.

The relation between w_i and $[O_2]$ is a linear one. Non-uniform distribution of dissolved oxygen in rubber occurs when, as a result of the strongly activated process, the rate of inhibited oxidation is limited by the rate of diffusion of oxygen in the rubber. Both purely chemical and purely physical factors can be instrumental in activating initiation. The former include a number of chemically active oxygen transfer agents (for example, salts of heavy metals), which lower the activation barrier of initiation. The latter include the action of mechanical factors discussed in another article in the same series of investigations.

These processes can also be studied by investigating the kinetics of consumption of the inhibitor.

REACTIVITY OF ELASTOMERS AS RELATED TO THEIR STRUCTURE

Using the inhibition method, we were able to determine the reactivity of any particular type of rubber and discover the relation between its activity and the structure of the rubber molecule. The solution of this problem has not yet been obtained for want of an appropriate method of investigation. Literature data are uncertain and contradictory⁵. By studying the influence of the structure of different types of rubber which do not contain negative substituents on the rate of inhibited oxidation at various temperatures, we established the following facts.

1. The rate of consumption of inhibitor during the oxidation of natural rubber (pale crepe), gutta-percha, butadiene rubbers and a styrene-butadiene copolymer, is practically independent of the length of the molecular chain,

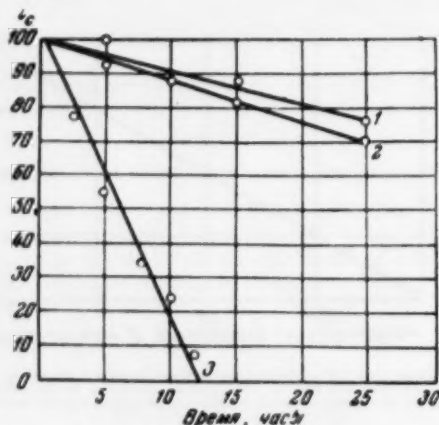


Fig. 4.—Kinetics of consumption of phenyl-2-naphthylamine during oxidation of sodium-butadiene rubber under various partial oxygen pressures. 1.—10 mm. Hg; 2.—200 mm. Hg; 3.—760 mm. Hg. Temperature 120° C. Initial inhibitor content 12.5 millimoles per l.; t : Content of free inhibitor in percentage of initial content. The abscissa indicates the time in hours.

spatial configuration, presence of aromatic rings, etc. but does depend directly on the content of double bonds in the main chain of the polymeric molecule.

2. The linear course of the consumption of phenyl-2-naphthylamine is evident in all cases (Figure 5), but the rate of initiation varies; this gives reason to think that the rate of initiation depends directly on the molecular structure of polymers. If one chain link, containing one aliphatic double bond, is assumed for each mole of rubber, and the relation of the initiation constant to the double-bond content in the main chain of the rubber molecules is derived⁶, it becomes evident that the relation is practically linear. It follows from this that the rate of initiation does not depend on the presence of double bonds in the side chains.

The energy of activation of inhibited oxidation at a double bond of the main chain is 21–23 kcal. per mole (derived from the inhibition data), the energy of activation of initiation at a side chain in butadiene rubbers (calculated from data on autocatalysis) is 26–28 kcal. per mole. This difference of the activation

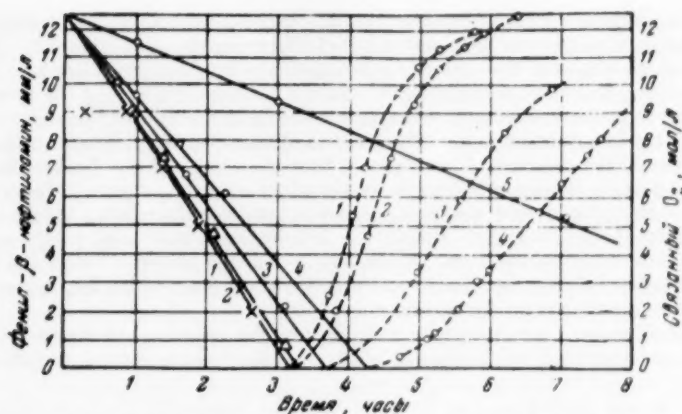


Fig. 5.—Kinetics of consumption of phenyl-2-naphthylamine and curves of the combination of oxygen after complete consumption of inhibitor. Temperature 120° C. Initial concentration 12.5 millimoles per l. 1.—Gutta-percha hydrocarbon; 2.—Natural-rubber hydrocarbon; 3.—Butadiene-styrene rubber; 4.—Butadiene rubber containing 60% double bonds in main chain; 5.—Butadiene rubber, containing 20% double bonds in main chain. The left-hand ordinate indicates the phenyl-2-naphthylamine content in millimoles per l.; the right-hand ordinate indicates the combined oxygen in moles per l.; the abscissa indicates the time in hours.

barriers of oxidation of the double bonds in the main and side chains of a rubber molecule is one cause of the inertia of the latter in the case of inhibited oxidation.

The inhibited oxidation of saturated polymers and polymers containing a very small proportion of double bonds is quite distinctive.

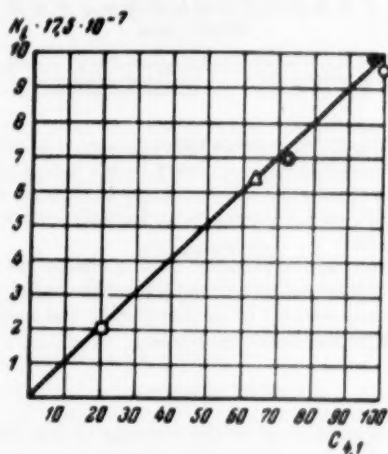


Fig. 6.—Relation between the initiation constants (K_i) and the content of double bonds in the main chains of polymer molecules ($C_{d,1}$):

- Gutta-percha hydrocarbon
- Natural rubber hydrocarbon
- Butadiene-styrene rubber
- △—Butadiene-styrene rubber containing 60% double bonds in the main chains
- Butadiene rubber containing 20% double bonds in the main chains

The kinetic curves of consumption of phenyl-2-naphthylamine during the oxidation of polyisobutylene and of Butyl rubber are shown in Figure 7. As is seen in the diagram, the curves of consumption of inhibitor show breaks. It is interesting that the consumption of inhibitor becomes less beyond the break in the curve in the case of polyisobutylene, whereas in the case of Butyl rubber it continues at a reduced rate. The position of the reversion depends on the experimental temperature. It was shown that the course of the broken line is parallel to the change of molecular weight of the oxidized polymer. Investigation of this phenomenon makes it possible to establish the relation between the stability of a chain and its length. A definite mean molecular weight corresponds to each temperature. From this it may be concluded that the long chains enter into the reaction sooner than the short ones, which are, in general, more stable than the long chains.

After stable chain lengths are reached in the oxidation of Butyl rubber, oxidation continues at the double bonds. At 110° C the rate of oxidation at

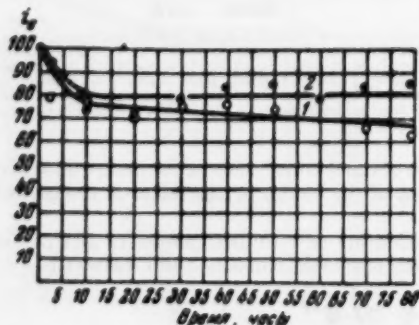


Fig. 7.—Kinetics of consumption of inhibitor during oxidation of Butyl rubber (curve 1) and polyisobutylene rubber (curve 2). Temperature 120° C. 0.5% Phenyl-2-naphthylamine was added; I , Content of free inhibitor in percentage of initial content. The abscissa indicates the time in hours.

ordinary bonds of Butyl rubber is seven times greater than at the double bonds. However, since the concentration of ordinary bonds in this polymer is 50 times greater than that of double bonds, the constants of the rate of inhibited oxidation of the latter are $50/7 = 7.1$ times greater than the corresponding constants of oxidation of the former.

It is worthy of note that the presence of long chains (which are characterized by the presence of internal stress) leads to such a weakening of the C—C bonds that, with a small content of double bonds, the reaction with oxygen takes place principally at the ordinary bonds.

CONCLUSIONS

1. The oxidation of elastomers in the presence of true inhibitors, of which secondary aromatic amines are an important class, is for practical purposes an initiation reaction and primary oxidation of the chains is possible only to a slight degree.

2. Inhibited oxidation (initiation) is fundamentally distinct from autocatalytic oxidation.

3. The method of study of inhibited oxidation (initiation) consists in the study of the consumption of inhibitor, while the rate of this process is equal to either the proportional rate of initiation or the constancy of the concentration of dissolved oxygen in the entire mass of the rubber film or specimen studied.

4. In the inhibited oxidation of different types of rubber, the rate of initiation is practically constant for each temperature. The activation energy of the reaction is equal to 22.6 kcal. per mole, and is independent of the nature of the polymer in the absence of electrically negative substituents in the polymer.

5. In the case of strongly activated nitration, the diffusion of oxygen in the rubber may have a retarding influence. Then the concentration of dissolved molecular oxygen $[O_2]$ differs at different depths below the surface. The relation of the rate of consumption of inhibitor w_i to the concentration of oxygen is a straight-line function, i.e., $w_i = A[O_2]^n$; at 120° C, $n = 0.5$.

6. The reactivity of rubber hydrocarbons with respect to molecular oxygen and certain other chemically active agents is determined principally by the content of double bonds in the main chains of the molecules of the polymers. Marked structural differences, such as degree of polymerization, spatial configuration, presence of aromatic rings, etc., have practically no influence on the rate of inhibited oxidation.

7. The absorption of oxygen by the double bonds of the side chains of butadiene rubbers has a much higher activation barrier (27–28 kcal. per mole); consequently, the double bonds are practically inactive during the inhibited oxidation of elastomers.

8. The oxidation of polyisobutylene in the presence of phenyl-2-naphthylamine is characterized by the presence of a temperature threshold, below which initiation does not take place. The directly related change of molecular weight and consumption of inhibitor indicate that destruction of the polymer continues until a constant molecular weight is reached.

9. The inhibited oxidation of Butyl rubber is characterized by the simultaneous progress of two rates of oxidation. The first is the rate of oxidation of the chains, which do not reach a constant weight; the second is the rate of absorption of oxygen at the double bonds.

In both polyisobutylene and Butyl rubber, the ordinary bonds of the long chains are considerably weakened. Since the concentration of ordinary bonds in Butyl rubber is much higher than the concentration of double bonds, the rate of oxidation of the former is greater than the rate of oxidation of the latter.

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TEST OF THE APPLICABILITY OF DIELECTRIC LOSS MEASUREMENTS TO THE STUDY OF THE AGING OF PURE-GUM RUBBER MIXTURES *

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INTRODUCTION

The usual means of determining the aging characteristics of vulcanized rubber is to measure either the loss of tensile strength during aging in an oxygen bomb or in a Geer oven or to measure the oxidizability of the vulcanizate.

Since aging is essentially an autoxidation phenomenon, it might be expected that one effect would be the formation of polar groups. If so, the presence of these groups should be readily detected by measurements of the dielectric losses at radio frequencies. This method has the additional advantage over tensile strength measurements that the samples are not destroyed.

In view of this, we have studied changes of the dielectric loss factor of vulcanizates during aging to ascertain whether this method is useful as a supplementary test to the other two aging tests.

THE DIELECTRIC ABSORPTION OF HIGH POLYMERS

The behavior of many elastic high polymers when placed in an alternating electric field of constant frequency is similar to that of polar liquids. For example, with rise of temperature, the dielectric constant increases, while the dielectric loss passes through a maximum.

The theory of Debye makes it possible to explain this phenomenon. This theory is based on the concept of "dielectric viscosity", which characterizes the resistance of the surrounding medium to the rotation of polar groups in the dielectric under the influence of the dielectric field.

The temperature corresponding to the maximum absorption makes it possible to estimate the dielectric viscosity for any given frequency. The height of the maximum, $\tan \delta_m$, is a direct function of the concentration and of the electric moment of the groups.

Finally, the magnitude of the temperature interval within which electric absorption is appreciable depends on the distribution of the relaxation times of the dipoles and, consequently, on the differences between their different molecular structures¹.

With respect to rubber which has not been aged, it is not polar when in the raw state, but is made polar by vulcanization. It is generally assumed that this change of polarity is due to the chemical fixation of sulfur during vulcanization². Sulfur combined in intramolecular form would, moreover, be to a high degree responsible for the dielectric losses in vulcanized rubber, whose dipoles would

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TABLE I

	I	II	III
Crepe rubber	100	100	100
Sulfur	2	3	2
Mercaptobenzothiazole (MBT)	—	—	1
Diphenylguanidine (DPG)	1	—	—
Tetramethylthiuram disulfide (TMT)	—	0.3	—
Stearic acid	1	0.5	1
Zinc oxide	5	2	5
Optimum time of vulcanization at 143° C (min.)	65	30	35

be formed by heterocycles located in random fashion along the polyisoprene chains³.

METHOD AND APPARATUS

The resonance method was used, for, by this means, the loss factor, $\tan \delta_m$, of the rubber sample can be determined by detuning a circuit in which the condenser unit is mounted in parallel. The latter is a double condenser, without guard electrode, whose dielectric comprises two rubber layers, $60 \times 5 \times 1$ mm. in size, located on each side of a nonoxidizable central electrode. The whole assembly is placed in a cylindrical case which constitutes the second electrode. This latter is grounded. A Dewar flask containing liquid nitrogen makes possible, by means of a heating resistor, the maintenance of any equilibrium temperature within a very broad range⁴, viz., -100° to 80° C. All measurements of the dielectric loss factor were made consistently at 120 kilocycles per second.

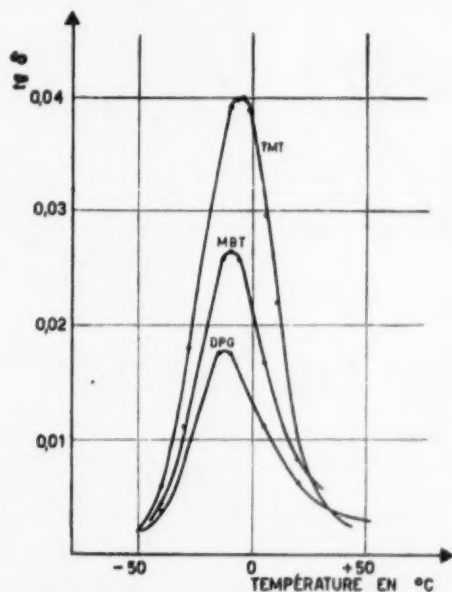


FIG. 1.—Absorption curves of vulcanizates before aging. Frequency 120 kilocycles per second. The ordinate indicates $\tan \delta_m$. On the curves, TMT is tetramethylthiuram disulfide, MBT is mercaptobenzothiazole, and DPG is diphenylguanidine.

EXPERIMENTAL RESULTS

Three mixtures were used in the experiments, as shown in Table 1. They contained only compounding ingredients required for vulcanization, and no antioxidant.

Figure 1, which represents the unaged vulcanizates, shows that the three mixtures differed greatly in their concentration of polar groups. According to Schallamach³, mixture II (tetramethylthiuram disulfide), which should contain a higher proportion of sulfur in the intramolecular form, should also have a

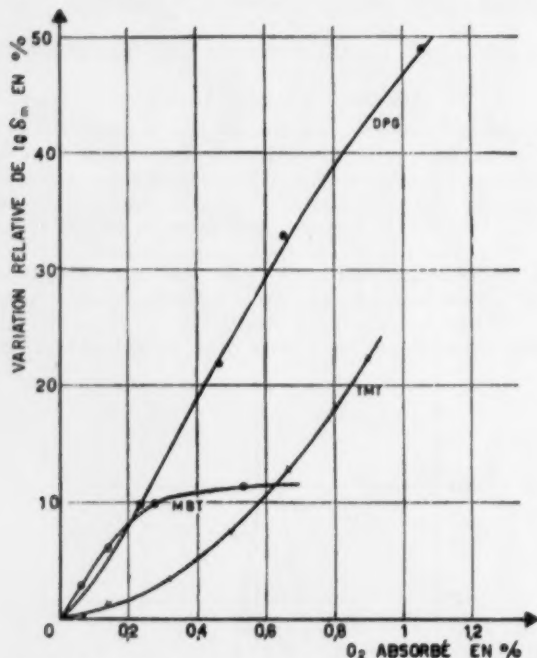


FIG. 2.—The change of $\tan \delta_m$ as a function of the percentage of oxygen absorbed at 80° C. Frequency 120 kilocycles per second. The abscissa indicates the percentage by weight of molecular oxygen absorbed; the ordinate the percentage increase of the $\tan \delta_m$ value. TMT, MBT, and DPG are the same as in Figure 1.

relatively high dielectric viscosity. This was, in fact, found to be true, since the maximum loss was at a somewhat higher temperature.

TESTS WITH THE DUFRAISSE MANOMETER

In a first series of tests, the oxidizability of the three mixtures was measured with a Dufraisse manometer by the usual technique. At 80° C the hourly rise of the mercury column was found to be: mixture I (diphenylguanidine) 55 mm.; mixture II (tetramethylthiuram disulfide) 24 mm.; mixture III (mercaptobenzothiazole) 4 mm.

Mixture III was, therefore, characterized by its slow rate of absorption of oxygen, compared with the much faster rates of mixtures I (diphenylguanidine) and II (tetramethylthiuram disulfide).

In a second series of experiments, the influence of the absorption of oxygen on the maximum loss, $\tan \delta_m$, was studied. To this end, a strip prepared for the dielectric tests was placed in each cell of the manometer and folded in a V-shape in such a way as to expose two surfaces to oxygen, in all cases at 80° C. Furthermore, in order to determine the percentage of oxygen absorbed by a sample (of known weight), the volume of oxygen absorbed, converted to normal temperature and pressure, was calculated as a function of the height of the mercury in the manometric tube.

Figure 2, which shows the relative change of $\tan \delta_m$ as a function of the oxygen absorbed, demonstrates that the effect of absorbed oxygen is to increase the concentration of polar groups in a vulcanizate. The course of the curves indicates that this increase depends, in turn on the character of the vulcanizate,

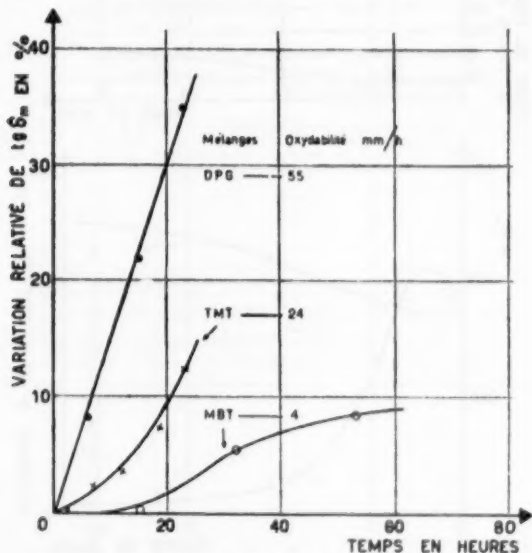


Fig. 3.—The change of $\tan \delta_m$ as a function of the time of exposure to oxygen at 80° C. Frequency 120 kilocycles per second. The abscissa indicates the time in hours; the ordinate the percentage increase of the $\tan \delta_m$ value.

and that it tends toward a definite limiting value in the case of mixture III (mercaptobenzothiazole).

In addition to increasing the polar groups, oxidation increases slightly the temperature of maximum absorption and also broadens the curves of dielectric absorption. Finally, Figure 3 shows the $\tan \delta_m$ values as a function of the time of exposure to oxygen. Mixture III (mercaptobenzothiazole) is characterized by an increase of the dielectric absorption which is decidedly slower than the increases of the other two mixtures.

AGING TESTS IN A GEER OVEN WITH SEPARATE COMPARTMENTS

Having found out from the preceding tests that oxidation increases the polarity of vulcanizates, it seemed probable that aging in a Geer oven would

lead to the same effect. In order to avoid all risk of contamination, the oven was divided into separate compartments by means of metal shells in which only test-specimens of the same vulcanizate were placed in any individual compartment. The losses of tensile strength and the $\tan \delta_m$ values were measured simultaneously at definite time intervals.

Figure 4 shows the changes of tensile strength, of $\tan \delta_m$, and of the temperature of the maximum loss for Mixture I (diphenylguanidine), which is characterized by its relatively rapid deterioration. For example, by aging for seventeen days, the tensile strength was greatly reduced and the $\tan \delta_m$ value

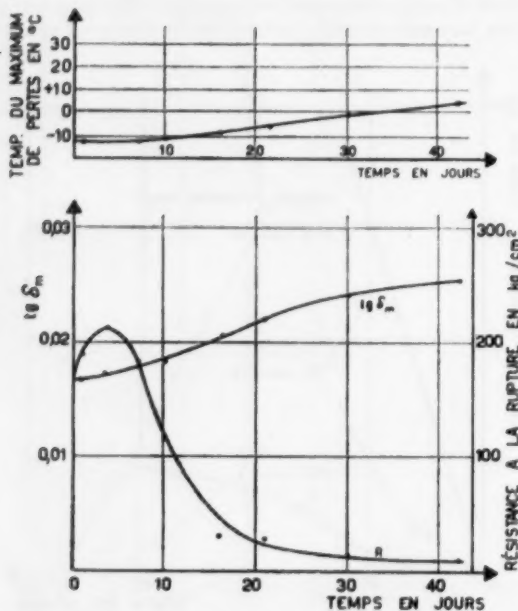


Fig. 4.—Aging of Mixture I (diphenylguanidine) in a Geer oven at 70° C. Frequency 120 kilocycles per second. In the lower graph, the abscissa indicates the time in hours; the left-hand ordinate the $\tan \delta_m$ value; the right-hand ordinate the tensile strength in kg. per sq. cm. In the upper graph, the abscissa indicates the time in hours; the ordinate the temperature in ° C of the maximum loss.

tended toward a limiting value. In addition, the temperature of maximum loss increased as an almost linear function of the time of aging.

Figure 5 shows that aging in a Geer oven leads also to a broadening of the curve of absorption as a function of the temperature.

According to Figure 6, aging of Mixture II (tetramethylthiuram disulfide) leads to the same phenomenon as that observed with Mixture I (diphenylguanidine). Also there is a similar broadening of the absorption curve.

Finally, Figure 7 shows that Mixture III (mercaptobenzothiazole) deteriorates less rapidly than the other two mixtures, and that the increase of $\tan \delta_m$ is, consequently, very slow. The increase of the temperature of maximum loss is itself greatly reduced in this case.

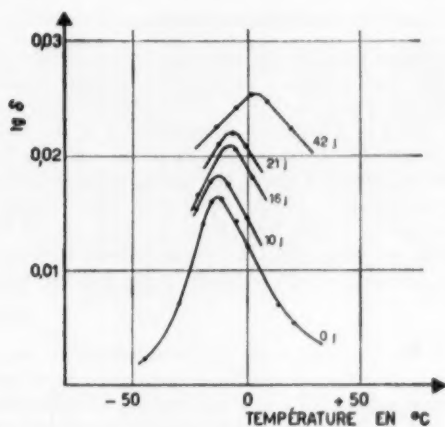


FIG. 5.—Absorption curves of Mixture I (diphenylguanidine) after aging in a Geer oven at 70° C. Frequency 120 kilocycles per second. The abscissa indicates the temperature in ° C; the ordinate the $\tan \delta_m$ value. The numbers on the five curves indicate the numbers in the Geer oven.

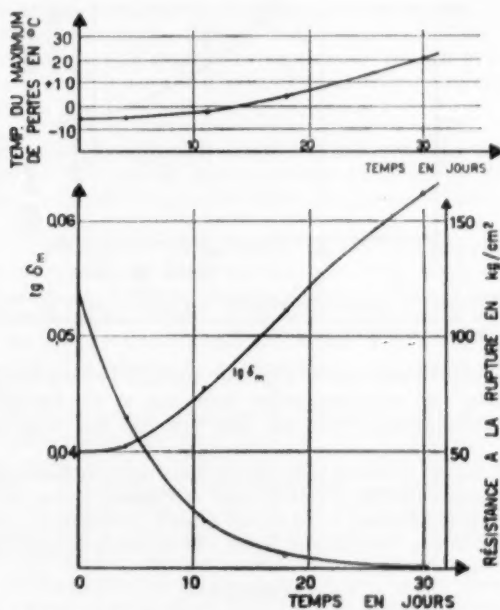


FIG. 6.—Aging of Mixture II (tetramethylthiuram disulfide) in a Geer oven at 70° C. Frequency 120 kilocycles per second. In the lower graph, the abscissa indicates the time in hours; the left-hand ordinate the $\tan \delta_m$ value; the right-hand ordinate the tensile strength in kg. per sq. cm. In the upper graph, the abscissa indicates the time in hours; the ordinate the temperature in ° C of the maximum loss.

SULFUR CONTENT

In order to determine whether the increase of combined sulfur content at the beginning of aging may influence the increase of polar groups, Mixture III (mercaptobenzothiazole) was undercured (which should mean low oxidizability) and was then aged alone in a separate compartment of the Geer oven. This test showed that, in spite of a notable increase of the combined sulfur ((11 per cent increase) at the beginning of aging, the $\tan \delta_m$ value and, consequently, the polarity remained unchanged. In the same way, the increase of the tensile strength which took place at the beginning of aging in the Geer oven with Mixtures I (diphenylguanidine) and III (mercaptobenzothiazole) do not represent any particular anomaly in the changes of the $\tan \delta_m$ value during aging (see Figures 4 and 7).

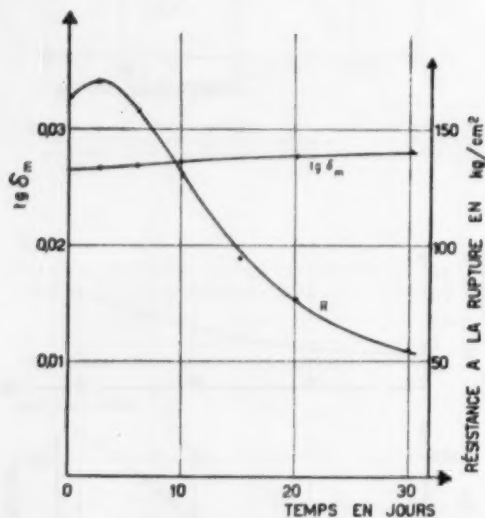


FIG. 7.—Aging of Mixture III (mercaptobenzothiazole) in a Geer oven at 70° C. Frequency 120 kilocycles per second. The abscissa indicates the time in days; the left-hand ordinate the $\tan \delta_m$ value; the right-hand ordinate the tensile strength in kg. per sq. cm.

It would seem that these results might be explained on the assumption that, with the foregoing two mixtures, sulfur combines at the beginning of aging chiefly in the intermolecular form, and that this does not cause any dielectric absorption.

Moreover, it should be noted that the curves of aging in the Geer oven show, for the electric measurements, a rather rapid rectilinear course, and this makes it possible to compare different vulcanizates after a much shorter period of aging than can be done in any comparison by tensile strength measurements.

CONCLUSIONS

Measurement of the dielectric properties of rubber at radio frequencies remains a somewhat delicate operation and requires special apparatus. It can, therefore, hardly be regarded as a practical aging test at the present time. On

the contrary, from the viewpoint of research, it may be found to be a particularly simple means of obtaining direct indications of the mode of combination of oxygen with rubber when the means of protection of the rubber against oxygen is altered, e.g., by antioxygenic agents and deactivating agents.

Although at present limited to a means of estimating the degree of polarity and of the mean obstruction of the oxygen-carrier groups, the information obtained by the method should, in fact, be of unquestionable value in a field where classic methods of analysis are, in general, not applicable.

This leads next to the question whether the results of the dielectric tests of the particular unprotected vulcanizates chosen for this preliminary study should, or should not, be regarded as an encouraging basis for further work.

Three general observations seem to give affirmative support to the potential value of the test.

(1) The three vulcanizates which were tested rated in exactly the same order when they were compared on a basis of rate of increase of dielectric absorption, of oxidizability (judged by the Dufrasse manometer, as shown in Figure 3), and of decrease of tensile strength in the Geer oven (Figures 4, 6, and 7).

(2) Oxygen combined with rubber in the polar form has an influence only on the increase of dielectric absorption during aging, in the sense that it is not impeded by post-vulcanization phenomena.

(3) In contrast to the Geer oven and oxidizability tests, the electrical testing method reveals clearly the way in which oxygen combines with rubber according to the type of accelerator present in the mixture. Thus, the increase of absorption with diphenylguanidine as accelerator is greater than with tetramethylthiuram disulfide or mercaptobenzothiazole for a given percentage of combined oxygen (see Figure 2).

If can fairly safely be affirmed, in addition, that the final stages of oxidation of the vulcanized Mixture III (mercaptobenzothiazole) are characterized by the formation of groups which, on the whole, are less polar than at the beginning of oxidation (see Figure 3).

These facts are evidently not sufficient to explain the complex mechanism of the oxidation reactions, but they may serve as a useful guide in the acceptance of some particular one of the many hypotheses which have been advanced for the general consideration of the chemist. Chemists are, for example, justified in assuming, by analogy with the effects of sulfur, that strong polarity indicates chemical fixation of oxygen in the intramolecular form rather than in the intermolecular form.

The differences in the temperatures of maximum absorption and differences in the shape of the absorption curves as a function of the temperature would, on the contrary, appear to be hardly characteristic of the particular compositions of the mixtures. It is, nevertheless, interesting to note that, as a general rule, the aging of vulcanized rubber leads to a rise of the temperature of the maximum and, consequently, to an increase of the dielectric viscosity, which is itself due to obstruction and to the molecular potential barriers.

The broadening of the absorption curves proves, on the other hand, that the polar groups formed during aging have various structures, and this confirms recent investigations, according to which oxidation results in the formation of various functional groups, including, for example, hydroxyl, acidic, aldehydic, ketonic, etc., groups.

Finally, measurement of the dielectric losses would seem to offer new possibilities for the study of the aging of vulcanizates. The importance of the method lies in particular in the fact that it offers a means of estimating the degree of polarity of the oxidation products. It should, then, by good fortune, serve to add to the already classic criteria of aging, i.e., oxidizability, stress relaxation, and losses of mechanical properties when the different mechanisms of aging are to be differentiated.

SUMMARY

The measurement of the dielectric properties at radioelectric frequencies requires a technique and apparatus which are too delicate to serve at the present time as a practical test of the aging of vulcanized rubber. On the other hand, from the viewpoint of research, the dielectric method should furnish valuable data on the way in which oxygen tends to combine with rubber according to the particular conditions of aging.

Thus, it has been found in aging tests of three different types of vulcanizates containing no protective agent that there is an increase of polarity, which in some cases great, an increase of the dielectric viscosity, and a broad distribution of polar groups, formed by oxidation, between the different types of structures.

The dielectric absorption leads in particular to the same classification of vulcanizates as do the classic methods of measuring oxidizability and decrease of tensile strength. Finally, in addition, measurement of the dielectric absorption makes possible the estimation at a high level of sensitivity of the degree of polarity of oxidation products.

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MECHANICAL ACTIVATION OF THE INITIATION OF OXIDATION OF ELASTOMERS *

A. S. KUZMINSKIĬ, M. G. MAIZELS, AND N. N. LEZHNEV

In recent years the processes which cause the destruction of rubbers subjected to mechanical deformation have been explained by Aleksandrov, Kobeko, Kargin, Slonimskii, and other Soviet scientists. The work of Koshelev and his coworkers established that the inhibitor is consumed during the aging of rubber. However, there have been no studies of the relation between the mechanical and chemical factors which cause the destruction of vulcanized rubber. Various individual experiments by foreign investigators have not solved this problem. The failure of studies to throw any light on the relation of the rate of the chemical processes to the conditions of deformation of vulcanizates is due to a large degree to errors inherent in the method.

It is of particular importance that laws derived in studies of autocatalytic oxidation have often been applied to the case of inhibited oxidation, although these processes are different.

Until now there have been no studies of the relation of the rate of inhibited oxidation during repeated deformation to the conditions of such deformation. The question of the influence of the rate of inhibited oxidation on the change of the physical-mechanical properties of vulcanizates has also been neglected.

MECHANICAL ACTIVATION OF THE INITIATION OF OXIDATION PROCESSES

The study of the above-mentioned relations is extremely important, both theoretically and practically. As the authors have shown earlier¹, effectively inhibited oxidation at constant oxygen pressure can be regarded as limited only by the initiation process. The rate of consumption of inhibitor is a measure of the rate of initiation and a criterion for determining the rate of inhibited oxidation. This rate is constant, and so it is possible to calculate easily the corresponding constants of initiation, activation energy, etc., of unvulcanized and vulcanized rubbers when subjected to mechanical stress and when not subjected to such stress.

From a practical viewpoint, the study of inhibited oxidation is of primary importance, since unvulcanized and vulcanized rubber mixtures ordinarily contain an inhibitor (antioxidant) and their products are usually subjected to repeated deformations in use. This means that the rubber ages under conditions of inhibited oxidation and, at the same time, in a state of deformation. The inhibited process is also important in rubber technology, since certain manufacturing operations in which the material undergoes stresses are based on it, e.g., plasticization and reclaiming.

It was shown experimentally (Figure 1) that, at the very beginning of autocatalytic oxidation, the mechanical properties of vulcanizates change abruptly, resulting in a loss of valuable rubberlike properties.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Khimiya i Fiziko-Khimiya Vysokomolekul. Soedinenii*, Doklady 7-oi Konf. Vysokomolekul. Soedineniyam, pages 90-107 (1952).

Thus the technical use of rubbers is limited by the period of slow oxidation, which in practice is the period of the inhibited process.

The physical-mechanical properties also change gradually during this same period, as a result of changes in the structure of the rubber. The initial effect of these changes is evidently rupture of the hydrocarbon chains, due in unstressed specimens only to the decomposition of active peroxides which are

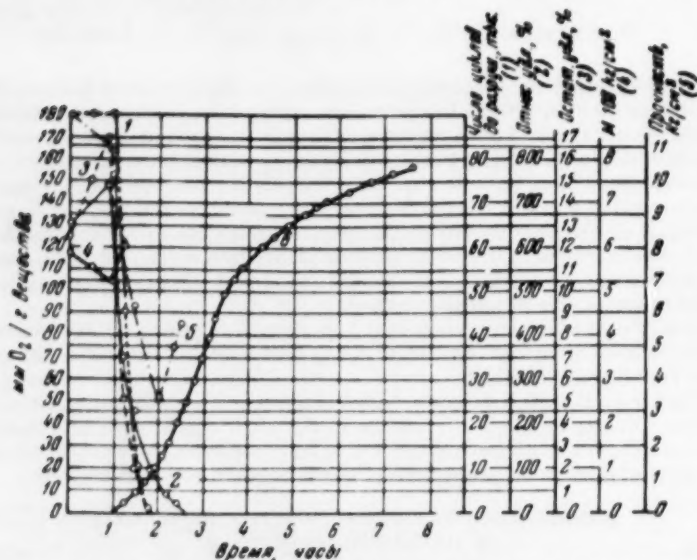


FIG. 1.—Change of physical-mechanical properties of vulcanizates of butadiene-styrene rubber as a result of oxidation: 1. Work capacity in 1000 cycles; 2. Relative elongation in per cent; 3. Residual elongation in per cent; 4. Stress at 100% elongation in kg. per sq. cm.; 5. Tensile strength in kg. per sq. cm.; 6. Curve of kinetics of oxidation. Temperature 120° C. The left-hand ordinate indicates the cc. of molecular oxygen per gram of substance. The five right-hand ordinates indicate (1) the number of 1000 cycles to destruction; (2) the percentage elongation at rupture; (3) the percentage residual elongation; (4) the modulus at 100 per cent elongation in kg. per sq. cm.; and (5) the tensile strength in kg. per sq. cm. The abscissa indicates the time in hours.

found as a result of the initiation of the reaction. The rate of formation of peroxide groups or initial active centers (n_0) is:

$$\frac{dn_0}{dt} = w_i = K_i[L][O_2]$$

where K_i is the initiation constant, $[L]$ is the concentration of chain linkages, each containing one aliphatic double bond. The molecular weight of such linkages is conventionally regarded as a "mole of the polymer".

The rate of their destruction during the reaction with the inhibitor (b) is:

$$w_a = -\frac{dn_0}{dt} = -\frac{db}{dt} = K_a[b][n_0]$$

It is assumed that the reaction of oxygen with the polymer and an active center with the inhibitor proceeds in the ratio 1:1. This is evidently true in the case of monofunctional antioxidants.

For the whole segment in the stationary state, $w_i = w_n$, i.e.,

$$K_i[L][O_2] = K_n[b][n_0] = -\frac{db}{dt} \quad (1)$$

then

$$[n_0] = \frac{K_i}{K_n} \cdot \frac{[L][O_2]}{[b]} \quad (2)$$

Since the product of $[L][O_2]$ under conditions of inhibited oxidation of rubbers at constant oxygen pressure is constant, it follows directly from Equation (2) that the equilibrium concentration of active centers is inversely proportional to the concentration of inhibitor. The higher $[n_0]$ is, the greater is the probability of spontaneous decomposition of the peroxide. Consequently, one would naturally expect that the change of mechanical properties of vulcanizates during inhibited oxidation would depend on the amount of inhibitor added, and the rate of its consumption, i.e., the value of w_i . The effect of the initial concentration of inhibitor was observed in our laboratory (Table 1).

The function w_i can be increased in several ways, independent of the influence of the type of rubber itself on the value of this function. Since K_i increases faster than K_n (initiation is a non-radical process and requires a higher

TABLE I
RELATION OF THE WORK CAPACITY OF VULCANIZATES OF BUTADIENE-
STYRENE RUBBER TO THE CONCENTRATION OF INHIBITOR
(Deformation system: frequency 250 cycles per min.; amplitude
50 per cent; temperature 20–22° C in air)

Concentration of inhibitor (%)	Work capacity (hours)	Work capacity (1000 cycles)
0.25	7.5	113
0.50	13.0	198
1.00	17.0	255

The results are the averages of 25 measurements at each concentration.

energy of activation than the reaction of a radical peroxide with inhibitor), $[n_0]$ in Equation (2) increases with the temperature when $[b]$ is constant. Consequently, the probability of oxidative rupture of the hydrocarbon chains increases. The w_i value can be increased by adding activators, i.e., oxygen transfer agents.

MECHANICAL ACTIVATION OF INITIATION DUE TO REPEATED DEFORMATIONS OF VULCANIZATES

The increase of w_i during the fatigue stressing of vulcanizates is particularly interesting. The curves of the kinetics of consumption of phenyl-2-naphthylamine during the oxidation of a vulcanized butadiene-styrene copolymer, not fatigued and fatigued by repeated elongation to 50 per cent of the initial length of the specimens at a deformation frequency of 250 cycles per minute, are shown in Figure 2. The composition of the vulcanizates was: rubber 95.6, tetramethythyuram disulfide 3, zinc oxide 1, and phenyl-2-naphthylamine 0.4 parts. The temperature of vulcanization was 143° C and the time was 60 minutes.

Since the tangents of the angles of inclination of the curves are $\frac{db}{dt} = w_i$; it is seen from Figure 2 that repeated deformation of vulcanizates activates the initiation reaction.

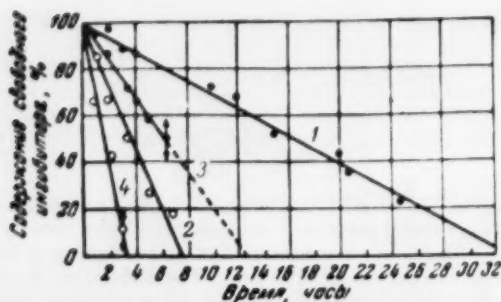


FIG. 2.—Kinetics of consumption of inhibitor during oxidation without deformation and during fatigue (amplitude 50 per cent; frequency 250 cycles per min.): 1. Without deformation (123°); 2. During fatigue (123°); 3. Without deformation (143°); 4. During fatigue (143°). The ordinate indicates the percentage content of free inhibitor; the abscissa indicates the time in hours.

In fact, the temperature relation of w_i for unvulcanized and vulcanized rubber subjected to mechanical stresses is less than that for the oxidation of stretched specimens. At an elongation of 50 per cent and frequency of 250 cycles per minute, the activation barrier is equal to 18.1 kcal. per mole, while, during the oxidation of unstressed vulcanizates, $E_a = 21.0$ kcal. per mole. The difference, $21.0 - 18.1 = 2.9$ kcal. per mole, is the gain obtained by converting the mechanical energy into chemical energy. Because the experiment was performed on thin films under thermostatic conditions, spontaneous heating of the films was practically negligible. The decrease of the energy of activation and increase of the rate of initiation result in an increase of the equilibrium concentration of active centers and the probability of rupture of the molecular chains.

This is one of the reasons why rupture of the specimens (indicated by arrows in Figures 2, 3, and 4) takes place long before the inhibitor is completely exhausted. The higher is the deformation, the larger is w_i and the sooner the specimen is ruptured (Figure 3).

The relaxation character of the deformation of rubber explains why the more severe are the deformation conditions, i.e., the greater the deformation or the

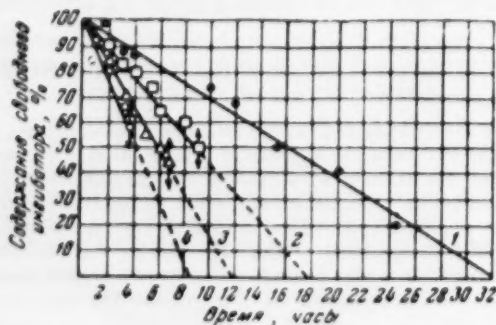


FIG. 3.—Influence of the amplitude of deformation on the kinetics of consumption of inhibitor during oxidation of fatigued vulcanizates. Temperature 123° C; frequency 250 cycles per min. 1. Without deformation; 2. Amplitude 25 per cent; 3. Amplitude 50 per cent; 4. Amplitude 75 per cent. The ordinate indicates the percentage content of free inhibitor; the abscissa indicates the time in hours.

higher the frequency, the greater is the activation effect (Figure 4). In accord with what was said earlier, an increase of w_i leads to rupture of the specimen in the presence of a high percentage of inhibitor. The relation of w_i to the elongation and frequency of deformation is nearly linear.

Kuzminskii and Lezhnev¹ showed that the rate of initiation of rubber which contains no electrically negative substituents is almost linearly dependent on the number of double bonds in the main chains of the rubber molecules. Mechanical stresses are also transmitted principally by the main chains; consequently the mechanical forces act in opposition to the valence forces and tend to rupture the hydrocarbon chain. The chemical bond is weakened, and this causes a decrease of the activation barrier of the initiation reaction. When the chain is stretched, some of its segments are subjected to mechanical stress. In these segments, the chain link which contains an aliphatic double bond passes the stage of activation, and only in the case of very energetic reactions is there purely mechanical rupture. In other cases, rupture of the chain is a result of the activated chemical reaction. The process, when subjected to a certain

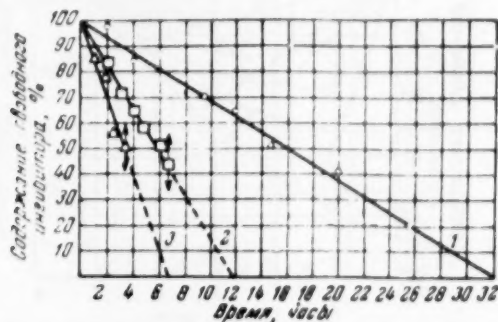


Fig. 4.—Influence of the deformation frequency on the kinetics of consumption of inhibitor during fatigue. Temperature 123° C; amplitude 50 per cent. 1. Without deformation; 2. Frequency 250 cycles per min.; 3. Frequency 500 cycles per min. The ordinate indicates the percentage content of inhibitor; the abscissa indicates the time in hours.

statistical distribution, indicates that the maximum number of ruptures is caused by the chemical reaction.

Periodic mechanical stresses cause an irregularity in the rate of the oxidation process, since different segments of the specimen are activated to different degrees.

Purely mechanical rupture is very improbable when rubbers undergo fatigue, since besides the probability of statistical distribution, indicated by direct experimental data, fragments of the chain—the free radicals—react with molecular oxygen with a low energy of activation (5–8 kcal. per mole). If we consider the experimental data and calculate the energy of activation of the supplementary process which takes place only as a result of activation, that is, E_a of the increment of the rate, Δw_i , which is due to the imposition of mechanical stresses on the vulcanizate of butadiene-styrene rubber ($\epsilon = 50$ per cent, frequency 250 cycles per min.), we obtain 16 kcal. per mole, that is, a value which is not characteristic of the reaction of oxygen with radicals.

The existence of a chemical process is evident graphically by a comparison of the work capacity of the above mentioned vulcanizates in nitrogen and in oxygen.

At 20° C, the work capacity in nitrogen with respect to that in oxygen is 2; at 60° C, 10; at 100° C, 105. The influence of oxidative destruction is evident.

MECHANICAL ACTIVATION OF INITIATION DURING PLASTICIZATION

Rubber is subjected to energetic mechanical reactions during plasticization. The mechanical stresses are incomparably greater than during fatiguing. In complete accord with the theory, the consumption of phenyl-2-naphthylamine during the plasticization of sodium-butadiene rubber under isothermic conditions follows a linear law. The rate of consumption of the inhibitor is much greater than during fatigue (Figure 5).

The temperature relation is, accordingly, much smaller. An approximate calculation for E_a at the friction ratio: 1:1.25, and clearance between the rolls of

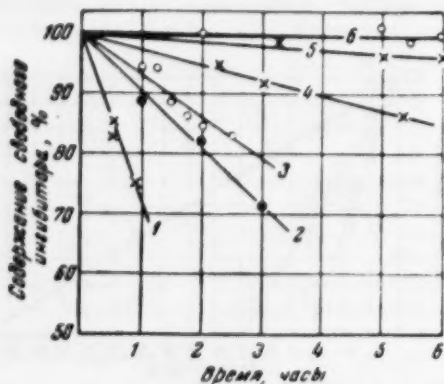


Fig. 5.—Kinetics of consumption of inhibitor during the oxidation of plasticized sodium-butadiene rubber: 1. Friction 1:1.5; Temperature 20° C; 2. Friction 1:1.25; temperature 80° C; 3. Friction 1:1.25; temperature 70° C; 4. Unplasticized rubber, temperature 90° C; 5. The same, temperature 70° C; 6. The same, temperature 20° C, thickness of layer of rubber in all cases 150 μ . The ordinate indicates the percentage content of free inhibitor; the abscissa indicates the time in hours.

0.1 cm. gives 8.46 kcal. per mole, using rolls 145 \times 290 mm., with the large roll making 20 revolutions per minute.

This value makes it possible to regard the probability of purely mechanical and oxidative processes as comparable, and, hence, the formation of free radicals as a result of the mechanical rupture of the chains is quite possible. On the other hand, the influence of the rate of diffusion is evident; consequently, the rate of oxidation varies at different depths below the surface.

We have shown that, during the oxidation of thin films of sodium-butadiene rubber (30–40 μ) containing phenyl-2-naphthylamine, at various oxygen pressures, the rate of consumption of inhibitor (w_i) is also a linear function of time. However, the relation between this rate and the value of p_{O_2} is not linear, but exponential; i.e., $w_i = A[O_2]^n$, where A and n are constants, and n at 120° C is $\frac{1}{2}$.

The rate of oxidation of a homogeneous sheet of raw or vulcanized rubber at depth x is proportional to the rate of diffusion of oxygen, i.e.,

$$\frac{\partial[O_2]}{\partial t} = KD \frac{\partial^2[O_2]}{\partial x^2} \quad (3)$$

according to Fisk's law; then, considering $w_i = w_i$, we have:

$$\frac{\partial^2 [O_2]}{\partial x^2} = \frac{A}{KD} [O_2]^n = K[O_2]^n \quad (4)$$

Regarding D as constant throughout the sheet and $n = 0.5$, by introducing limiting conditions, we can analyze function (4) in series. The limiting conditions are: (1) the oxygen concentration on the surface is equal to the solubility of oxygen in the given rubber, and (2) $\frac{\partial [O_2]}{\partial x} = 0$ at a depth, half the thickness of the sheet, oxidized from both surfaces.

The curves of the relation of the concentration of oxygen dissolved in sodium-butadiene rubber to the distance from the surface of the rubber at various depths are shown in Figure 6. Knowing the integral concentration of

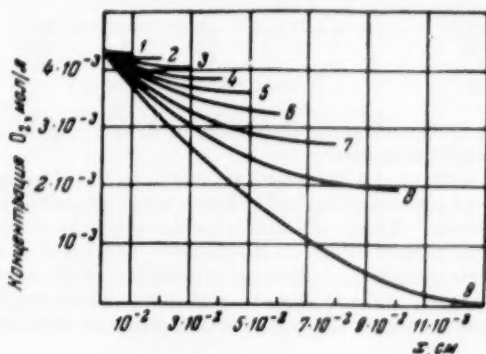


Fig. 6.—Curves showing the relation of $[O_2]$ concentration to the distance from the surface of the rubber, (x), for various thickness of sodium-butadiene rubber plasticized at friction 1:1.25 and temperature 120°C . Thickness of layer of rubber: 1.—0.01 mm.; 2.—0.2 mm.; 3.—0.3 mm.; 4.—0.4 mm.; 5.—0.5 mm.; 6.—0.6 mm.; 7.—0.8 mm.; 8.—1 mm.; 9.—1.5 mm. The ordinate indicates the concentration of molecular oxygen in moles per liter; the abscissa indicates the distance x from the surface in cm.

oxygen, we can calculate the average constants of rate of inhibited oxidation during plasticization and the energy of activation, respectively.

EFFECT OF MECHANICAL ACTIVATION OR INITIATION ON THE CHANGE OF THE PRE-EXPONENTIAL FACTOR (A) IN THE ARRHENIUS EQUATION

It is interesting that, with an increase of intensity of mechanical reactions, with a large decrease of the energy of activation, a sharp decrease of the pre-exponential factor is also observed, as is seen in Table 2.

It follows from Table 2 that, under given conditions of plasticization, the specific rates of inhibited oxidation are only 130–180 times larger than the rates of oxidation of unplasticized rubber, while the energy of activation decreases to 14.4 kcal. per mole. The same phenomenon, but less pronounced, is observed during repeated stretching. E_a decreases to 2.9 kcal. per mole, whereas the specific rates increase only 2.2 times. This is caused by the sharp decrease of the pre-exponential factor during fatigue, 16 times, and during plasticization, 4.5×10^6 times.

TABLE II

CHANGE OF ENERGY OF ACTIVATION AND PRE-EXPONENTIAL FACTOR DURING MECHANICALLY ACTIVATED OXIDATION OF RUBBERS IN THE PRESENCE OF PHENYL-2-NAPHTHYLAMINE

(Initial concentration of inhibitor: 0.5 per cent)

Rubber		Temperature (° C)	$K_1 \cdot 10^2$ (l./mole/ sec.)	E_a (kcal./ mole)	A (l./mole)	
Sodium-butadiene rubber	Not subjected to mechanical action	70	0.47	22.6	9.1	10^4
		80	0.94	22.6	9.1	10^4
Vulcanized butadiene- styrene rubber	Not subjected to fatigue	123	28.0	21.0	83	10^4
		133	58.6	21.0	87	10^4
		143	122.80	21.0	100	10^4
Plasticized at friction 1:1.25		70	83.8	8.46	1.95	
		80	122.7	8.46	2.14	
Fatigue by repeated stretching to 50% of original length at 250 cycles/min.		123	76.7	18.1	50800	
		133	144.4	18.1	53300	
		143	273.4	18.1	63300	

Here is a case of dependence in the change of E_a and $\ln A$, mentioned many times in the scientific literature.

The differing activity of rubbers with respect to inhibited oxidation depends on the double bond content of the main chains, which are subjected to most of the mechanical stress. Kinetically this is indicated by the different values of the pre-exponential factors for different rubbers. The fall of A when stress is applied is evidently caused by a decrease of mobility of the stretched chains. This causes a reduction of the total number of contacts between free chain segments and oxygen molecules, although the proportion of effective contacts increases.

CONCLUSIONS

1. This is the first study of the relation of uninhibited oxidation to the conditions of mechanical stress of vulcanized and unvulcanized rubber. Inhibited oxidation is confined to the initiation process.

2. At the end of the inhibition period and in the earliest stages of autocatalysis, the physical-mechanical properties of vulcanizates change sharply, and lose much of their technical value. In practice, one is nearly always concerned with inhibited oxidation, and, consequently, the study of this process is very important.

3. The rate of initiation of fatigued vulcanizates and plasticized rubber is determined by studying the kinetics of consumption of the inhibitor, which in the present work was phenyl-2-naphthylamine.

4. The uniform concentration of initial active centers is directly proportional to the rate of initiation (w_i) and inversely proportional to the concentration of inhibitor dissolved in the rubber. The probability of chemical rupture of the hydrocarbon chains increases with increase of w_i .

5. An increase of the rate of initiation or decrease of the concentration of inhibitor leads to an increase of the probability of oxidative rupture of the hydrocarbon chains. There is an increase of w_i when the temperature is increased, when oxidation catalysts are added, or when the hydrocarbon chain is subjected to mechanical stresses.

6. Repeated stretching or plasticization leads to a decrease of the activation barrier of the initiation reaction, since the mechanical forces counteract the forces of chemical combination. Owing to the relaxation character of deformation, an increase of severity of the conditions of stressing causes an increase of w_i .

7. Both the mechanically activated chemical reaction and the direct action of mechanical stresses can lead to rupture of test-specimens. In the case of fatigue, the probability of purely mechanical ruptures is small; during plasticization it is much larger.

8. With an increase of intensity of the mechanical reactions, and a large decrease of the activating energy of initiation, there is a simultaneous abrupt decrease of the pre-exponential factor. The decrease of E_a is functionally related to the decrease of $\ln A$.

9. The decrease of the pre-exponential factor when mechanical stresses are applied is evidently due to a decrease of mobility of the stressed chains. The total number of contacts decreases, while the proportion of effective contacts increases.

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PROTECTION OF NATURAL RUBBER AGAINST ATMOSPHERIC AGENTS. I. THE EFFECTS OF NICKEL DIBUTYLDITHIOCARBAMATE ALONE AND IN COMBINATION WITH PROTECTIVE AGENTS *

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INTRODUCTION

The effect of atmospheric agents on rubber has been the subject of numerous investigations, but in this work we shall confine ourselves to mentioning only a few. Most of the investigations have sought to explain, to duplicate, or to evaluate the changes in rubber brought about by the action of sunlight or atmospheric ozone. Among recent publications on the subject, those of Ford¹, Cuthbertson², Leigh-Dugmore³, Meynard⁴, and Smith⁵ may, in particular, be cited.

Methods of protection have been recommended⁶, but it can hardly be said that the problem has been resolved satisfactorily, particularly in the case of natural rubber.

The present investigation has, as its objective, the improvement of the resistance of vulcanized natural rubber when exposed to sunlight and to atmospheric agents. Other forms of aging have not been overlooked, and the attempt has been made to avoid or to minimize any losses of quality caused by heat or during natural aging in darkness which may result from the use of certain agents used for protection against light. The study was confined to the effects of one organic compound, viz., nickel dibutyldithiocarbamate (NBC), alone and in combination with antioxygenic agents, structuring agents, or deactivating agents⁷.

EFFECTS OF ATMOSPHERIC AGENTS

Let it be assumed that there are two types of degradation in the open air and that these are manifest by distinctly different effects. With respect to chemical degradation, it is uncertain whether this process involves one or two different phenomena, but, from the practical standpoint at least, two types of degradation are easily distinguishable by their different effects.

In agreement with Newton⁸ and with Crabtree⁹, the term "exposure cracking" seems preferable to "ozone cracking" for the degradation which is manifest by deep fissures parallel to one another and perpendicular to the direction of strain. These fissures appear when samples of rubber are kept in a state of tension in the open air. Fissure formation seems to depend primarily on the ozone content of the air, and light seems to play no part in the phenomenon, since such fissure formation takes place in the same way in darkness in artifi-

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ally ozonized air. The term ozone cracking may be a convenient one, but it is based on the supposition that this type of degradation is artificial and is necessarily dependent on the presence of ozone. However, it is quite possible that other agents, such as volatile peroxides, can have the same effects as ozone.

The other process of degradation depends primarily on the action of sunlight. Newton has proposed the term "light cracking" for the formation of a network of fissures which appear, without any particular alignment, on the surface of rubber which has become more or less resinified. This degradation, which is essentially a photochemical phenomenon, is the particular subject of study of the present work. The distinction has been made between the action of sunlight alone and that of sunlight in association with other effects of weathering.

In the first type of exposure tests, the rubber samples were exposed on a high open platform, where they were irradiated in frames ventilated laterally and covered by thin panes of glass which were kept scrupulously clean at all times. Simultaneous exposure to sunlight and to general weathering at the same time was effected by suspending sheets of rubber in the open air on the same platform. The time of exposure was twelve months, so that seasonable influences were taken into account and a mean annual radiation was obtained.

The arbitrary character and the uncertain reproducibility of all the experiments in open air was accepted as inevitable, but still it seemed preferable to rely upon this procedure, in view of there being no certain way of reproducing the active radiation of the solar spectrum otherwise.

A specially constructed lamp was tested, and it seemed to reproduce fairly precisely the effects of sunlight. However, because of not having established any correlation between the effects of artificial and natural radiation by a long series of experiments, these tests will not be discussed further at this time.

PREVIOUS INVESTIGATIONS OF NBC

Nickel dibutyldithiocarbamate (NBC) has been recommended as an agent for increasing the resistance to light of butadiene elastomers¹⁰, particularly of butadiene-styrene copolymers and polychloroprenes. Information contained in the patent literature and in the other publications cited indicates that NBC should be an equally effective agent in natural rubber, but aging tests in an oxygen bomb indicate, on the contrary, that it has a harmful effect on natural aging.

Preliminary experiments on cellular rubber¹¹, which is particularly sensitive to oxidation, showed the possibility of increasing the resistance of natural rubber to light. By the addition of NBC to latex, sponge-rubber products can be obtained which, in general, have much greater resistance to sunlight and weathering effects than that of corresponding products containing no NBC. On the contrary, addition of NBC to masticated rubber gives disappointing results. However, if, in addition to the NBC, dinaphthyl-*p*-phenylenediamine (DNPD), for example, is also added, a very pronounced "antilight" effect is again obtained.

More recently, Verbanc¹², in a study of the effects of nickel compounds in elastomers, found that NBC has a protective effect in synthetic rubbers, but that it has certain harmful effects in the aging of natural rubber, judged by conventional accelerated aging tests.

As a result of a comparison of the effects of new protective agents in different elastomers, Popp and Harrison¹³ classify NBC at the head as a protective agent

against light and against ozone. In some of the experiments, NBC was more effective than Santoflex-AW and than waxes used for the surface protection of rubbers.

Results described later confirm the sensitivity to heat of natural-rubber vulcanizates containing NBC which had been added during mixing. However, to make a reliable comparison between natural rubber and GR-S, account must be taken of the fact that most types of raw GR-S contain adequate amounts of particularly effective protective agents, which are, moreover, compatible with NBC. It will be shown later that the resistance of masticated rubber to heat

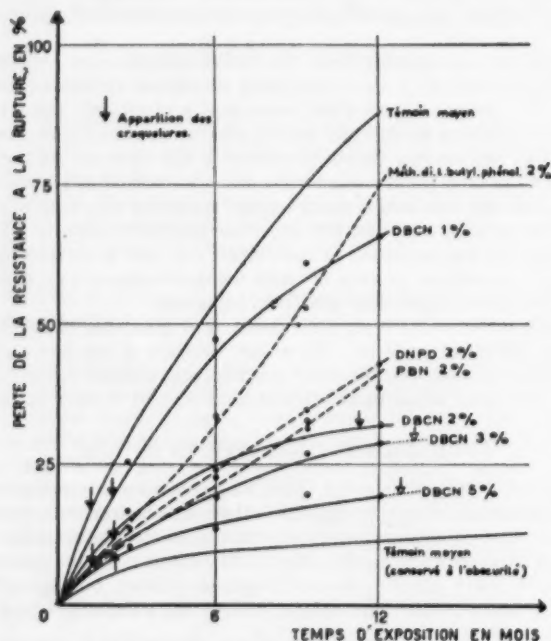


Fig. 1.—Latex-rubber vulcanizates. Loss of tensile strength by exposure to sunlight. The abscissa indicates the time of exposure in months; the ordinate the percentage loss of tensile strength. The vertical arrows indicate the time when cracks appeared. The uppermost curve represents the unprotected control vulcanizate exposed to sunlight; the lowest curve represents the same control vulcanizate stored in darkness.

can be considerably increased by the combined action of NBC and structuring agents, deactivators, or antioxygenic agents. Any comparison of GR-S and natural rubber is valid only if the comparison is of carbon-black vulcanizates containing the same proportion of carbon black and of carbon blacks having equivalent absorptive powers. This subject is dealt with in work which will be published separately.

Finally, the opinion of Hunter¹⁴ should be mentioned, who, in a review of the means of protecting elastomers according to a general plan, points out the lack of any effective means of combatting the effects of sunlight and of atmospheric ozone. He expressed the opinion, however, that new organic compounds, such as Santoflex-AW and complex organic derivatives of nickel, such as NBC, will

lead the way in the future to a more satisfactory solution of the problem of protecting elastomers against light and ozone.

TYPES OF VULCANIZATES TESTED

The experiments were carried out with vulcanizates prepared from latex and from dry-rubber mixtures. The experiments with rubbers containing reinforcing fillers, although of particular interest, will be described only briefly here, for they are to be the subject of a later publication.

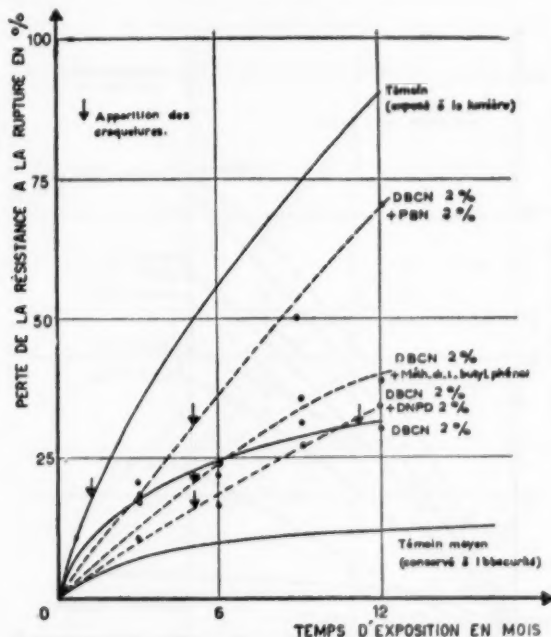


FIG. 1a.—Latex-rubber vulcanizates. Loss of tensile strength by exposure to sunlight. The abscissa indicates the time of exposure in months; the ordinate the percentage loss of tensile strength. The vertical arrows indicate the times when cracks appeared. The uppermost curve represents the unprotected control vulcanizate exposed to sunlight; the lowest curve represents the same control vulcanizate stored in darkness.

Vulcanizates prepared from latex are distinguished from corresponding vulcanizates prepared from dry-rubber mixtures by the molecular chain length and the character and extent of cross-linking. In addition, it is well known that the two types of mixtures do not show the same aging characteristics¹⁵. Furthermore, the mixing process and the nature of the accelerator system have a certain influence on the ultimate properties of the vulcanizates. A conventional method of vulcanization was, therefore, used for the two types of mixtures.

LATEX

Sheets, 2 mm. thick, were prepared by starting with ammonia-preserved latex concentrated by centrifugation. The latex was matured in the presence

of pancreatine and was then heat-sensitized by zinc oxide¹⁴. The mixture of latex containing the compounding ingredients in dispersion was gelled in aluminum molds by heating at 70° C in a water bath. The sheets were dried in open air at about 20° C, then were vulcanized in hot air for 1 hour at 90° C.

The composition of the blank (control) mixtures was: rubber (from latex) 100, sulfur 2, zinc diethyldithiocarbamate 1, and zinc oxide 3 parts by weight.

Similar sheets were prepared from dry rubber. In this case the base mixture was: smoked-sheet rubber 100 sulfur 3.5, mercaptobenzothiazole 0.5, stearic acid 0.5, and zinc oxide 6 parts by weight.

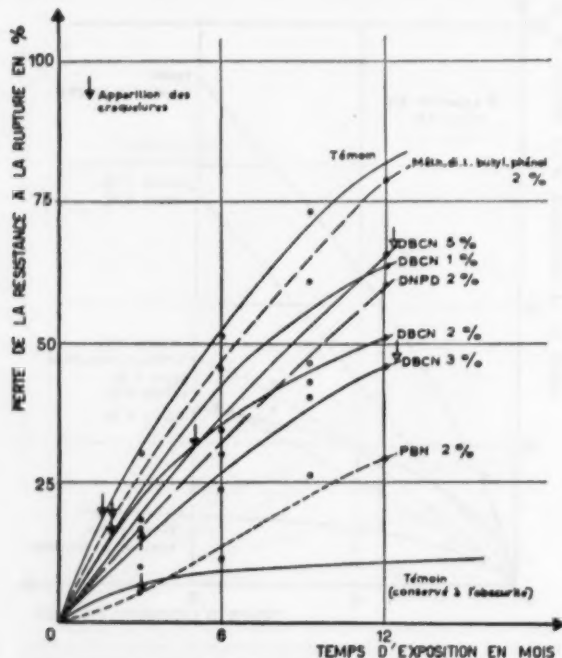


FIG. 2.—Latex-rubber vulcanizates. Loss of tensile strength by exposure to outdoor weathering. The abscissa indicates the time of exposure in months; the ordinate the percentage loss of tensile strength. The vertical arrows indicate the times when cracks appeared. The uppermost curve represents the unprotected control vulcanizate exposed outdoors; the lowest curve represents the same control vulcanizate stored in darkness.

The optimum state of cure, when press-vulcanized, was found to be 30 minutes at 135° C.

PROTECTION AGAINST CRACKING

The molded latex-rubber vulcanizates and the vulcanizates from dry-rubber mixtures were exposed in one series of experiments to sunlight and in another series to outdoor weathering. Samples in the form of solid sheets, 250 × 250 × 2 mm., were placed on a platform raised more than 20 meters above the ground level and completely exposed to solar radiation. The conditions of ex-

posure have been described above with respect to the difference between irradiation alone and the combined action of sunlight and outdoor weathering.

By periodical examination of the changing surface condition of the exposed samples, it was possible to determine the time necessary for cracks perceptible to the naked eye to appear. These times are indicated in Figures 1, 1a, 2, 2a, and 3 by the vertical black-pointed arrows. In cases when, at the termination of exposure to radiation, there was still no visible cracking, white-pointed arrows

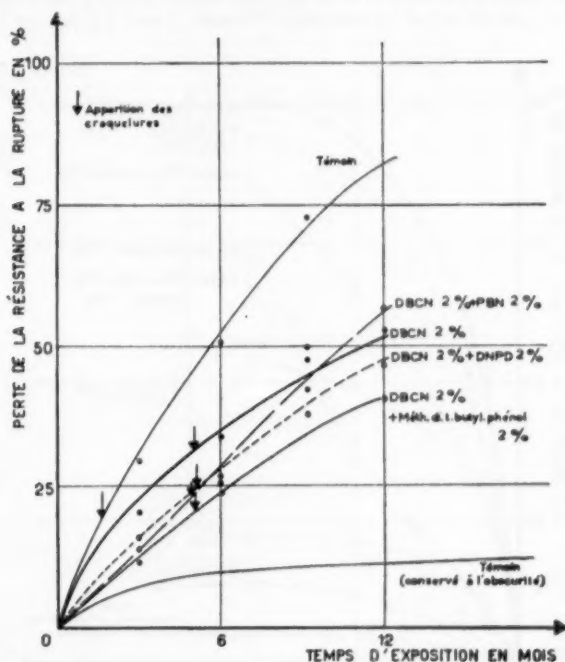


Fig. 2a.—Latex-rubber vulcanizates. Loss of tensile strength by exposure to outdoor weathering. The abscissa indicates the time of exposure in months; the ordinate the percentage loss of tensile strength. The vertical arrows indicate the times when cracks appeared. The uppermost curve represents the unprotected control vulcanizate exposed outdoors; the lowest curve represents the same control vulcanizate stored in darkness.

located beyond the zone of effective irradiation indicate that cracking became evident only after more than twelve months' exposure.

LATEX VULCANIZATES

The results are shown graphically in Figures 1 and 1a. The first cracks appeared rapidly on the unprotected control vulcanizate. It was of the order of one and one-half months, judged by five control samples. There was no significant difference between the effects of exposure to sunlight alone and exposure in the open to weathering.

A number of protective agents, chosen from the amine type of antioxygenic agents, were tested as reference agents. These included methyl-4-di(*tert.*-

butyl-2,6)phenol, *p*-benzyloxyphenol, phenyl- β -naphthylamine (PBN), an acetone-aniline reaction product, disalicylaethylenediamine, dinaphthyl-*p*-phenylenediamine (DNPD) and diphenyl-*p*-phenylenediamine (DPPD).

The influence of methyl-4-di(*tert*-butyl-2,6)phenol, phenyl- β -naphthylamine, and diphenyl-*p*-phenylenediamine are shown in Figure 1, from which it may be concluded that these agents have only a mild protective action, since cracking appeared from one and one-half to two and one-half months.

NBC was much more effective at concentrations above 1 per cent. There seemed to be a threshold of effectiveness between 1 and 1.5 per cent of NBC.

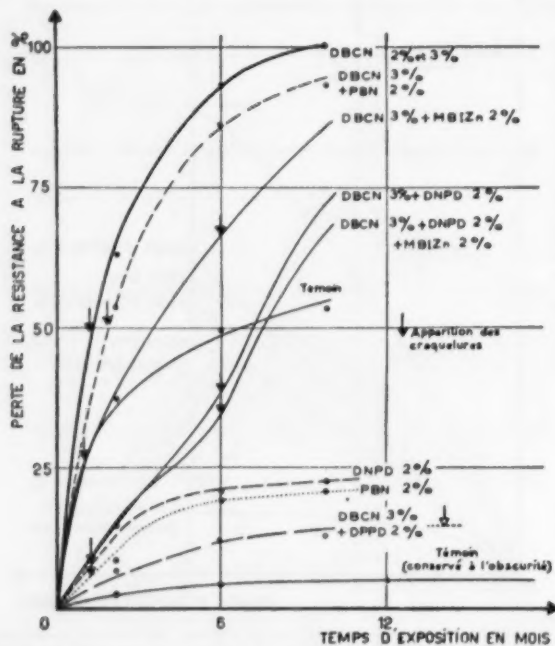


FIG. 3.—Dry-rubber vulcanizates. Loss of tensile strength by exposure to outdoor weather. The abscissa indicates the time of exposure in months; the ordinate the percentage loss of tensile strength. The vertical arrows indicate the times when cracks appeared. The curve designated Témoin is for the unprotected control vulcanizate exposed outdoors; the lowest curve is for the same unprotected vulcanizate stored in darkness.

Samples containing 2, 4, and 5 per cent of NBC showed practically no evidence of cracking after exposure to sunlight or to outdoor weathering for twelve months. Figure 2 shows, however, that the protective action against outdoor weather is somewhat less than against sunlight.


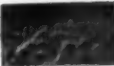







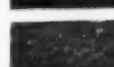
Combinations of NBC with the protective agents cited above did not lead to the increased resistance which was expected. In most cases, however, protection was sufficient for cracking not to become evident until about five months' exposure. This is then, a substantial increase of resistance in relation to the effects of antioxygenic agents alone. In any event, NBC is definitely more effective, even alone, than any of the combinations studied. These ob-

servations hold true in general of both exposure to sunlight and outdoor weathering. The results of the tests are summarized in Table 1.

VULCANIZATES OF DRY-RUBBER MIXTURES

Unloaded dry-rubber vulcanizates were studied in the same way as were the latex of the rubber vulcanizates. In this case, the similarity of the results of

TABLE 1

Protective agent	Condition of surface after exposure for 350 days	Condition of surface after exposure for 350 days	
None	Numerous relatively fine cracks; surface hardened	Fine deep cracks	
NBC (1%)	Fine cracks; pale- green glazed surface	Fine deep cracks; yellow coloration	
NBC (2%)	No visible cracks; green coloration	No visible cracks; except incipient cracking on the edges	
NBC (3%)	No visible cracks; green coloration	No visible cracks; very good state of preservation	
PBN (2%)	Fine cracks; browning	Fine deep cracks	
DNPD (2%)	Fine cracks, deeper than those with 2% PBN; browning	Fine cracks, but not deep	
Methyl di(<i>tert.</i> -butyl)phenol	Very fine cracks; no discoloration	Large deep cracks	
NBC (2%) + methyl di (<i>tert.</i> -butyl)phenol (2%)	No visible cracks	Fine peripheral cracks; good state of preservation	
NBC (2%) + PBN (2%)	Fine cracks; browning	Very fine cracks, not deep	
NBC (2%) + DNPD (2%)	Fine deep cracks; browning	Fine deep cracks	









exposure to sunlight and to outdoor weather was such that it seems sufficient to present only the results obtained by exposure to weathering outdoors.

An examination of Figure 3 will show the lack of effectiveness of NBC alone, because cracks appeared almost as soon as they did on the control vulcanizate containing no protective agent. Here too, a series of protective agents were tested, including methyl-4-di(*tert.*-butyl-2,5)phenyl, 2,2-methylene-di(4-methyl-6-*tert.*-butyl)phenol, saligenol, phenyl- β -naphthylamine (PBN), di-phenylamine-acetone reaction product, aniline-acetone reaction product, copper

phthalocyanine + antioxygenic agent, disalicylaethylenediamine, dinaphthyl-*p*-phenylenediamine (DNPD), diphenyl-*p*-phenylenediamine (DPPD), Nonox-EX, and zinc mercaptobenzimidazolate (ZMBI).

Some of the results are recorded as curves in Figure 3. When used individually, these compounds were relatively ineffective, and they retarded very little the appearance of cracks. But in combination with DNPD and ZMBI, NBC had a notable effect, and, with such combinations, cracks did not appear until about six months' exposure. Finally, it should be noted that a combination of NBC and DPPD had a great enough protective action for the samples

TABLE 2

Protective agent	Condition of surface after exposure to sunlight for 100 days	Condition of surface after exposure to sunlight for 365 days	
None	Network of large cracks on a resinified surface	Large deep cracks	
PBN (2%)	Cracking little different from that of the control; but notable browning	Cracks similar to those of the control	
DNPD (2%)	Rather extensive cracking and surface browning	Network of large deep cracks	
NBC (2%)	Fine cracks	Fine deep cracks	
NBC (3%) + PBN (2%)	Very numerous fine cracks and surface browning	Close network of cracks, not deep	
NBC (3%) + DNPD (3%)	Extremely fine cracks	Close network of cracks, not deep	
NBC (3%) + DNPD (2%) + ZMBI (2%)	Very slight cracking; good state of preservation	Close network of very superficial cracks	
NBC (3%) + DPPD (2%)	No cracks; excellent state of preservation, but marked browning	Barely perceptible cracks; good state of preservation	

to remain exposed for more than twelve months without any notable deterioration. Table 2 summarizes the most important results.

EXPOSURE OF SAMPLES UNDER TENSION TO OUTDOOR WEATHER

Exposure of vulcanizates under tension (elongations of 10–80 per cent) to outdoor weather gave results closely related to the effects of atmospheric ozone.

EXPOSURE OF VULCANIZATES UNDER TENSION TO OUTDOOR WEATHER

Exposure of vulcanizates under tension (elongations of 10–80 per cent) to outdoor weather gave results closely related to the effects of atmospheric ozone.

A few experiments were made with rubber-carbon black vulcanizates, the compositions of which were of the type in current use for the manufacture of glass insets. Figure 4 depicts the condition of samples after exposure, while elongated about 20 per cent, to outdoor weather for three months.

Three of the vulcanizates contained no paraffin wax. The other three vulcanizates were the same except that each contained 2 per cent of paraffin wax.

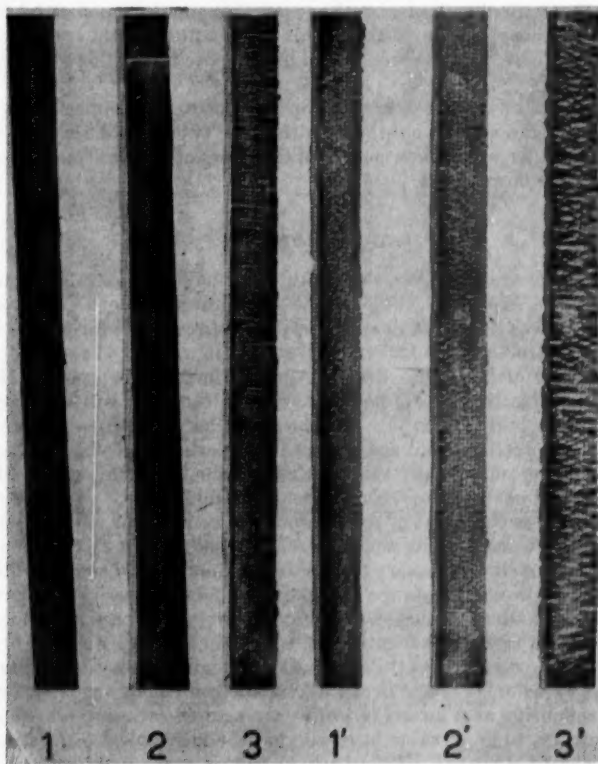


FIG. 4.—Rubber-carbon black vulcanizates exposed under tension to outdoor weather.

Vulcanizates containing paraffin wax.

1. NBC+DPPD
2. NBC+DNPD+ZMBI
3. No NBC+PBN+ZMBI

Vulcanizates containing no paraffin wax.

- 1'. NBC+DPPD
- 2'. NBC+DNPD+ZMBI
- 3'. No NBC+PBN+ZMBI

After exposure, the vulcanizates containing combinations of NBC and DPPD were in definitely better condition than were the unprotected vulcanizates. The presence of paraffin wax enhanced the protective effect of such combinations. Figure 4 shows that the vulcanizate protected by a combination of NBC and DPPD and at the same time by paraffin wax did not crack appreciably by exposure.

CHANGES IN THE MECHANICAL PROPERTIES OF THE VULCANIZATES
AS A FUNCTION OF THE TIME OF EXPOSURE

The beneficial effects of NBC and its combinations with other protective agents on exposure cracking are, in reality, important only because the mechanical properties of the vulcanizates are better preserved. Hence the necessity of studying, not only the changes of these properties during exposure to sunlight and to outdoor weather, but also the same changes during natural aging in darkness at ordinary temperature. This latter aspect of the question will be discussed elsewhere, and the results will be compared with those of accelerated aging tests.

The changes of the mechanical properties of the vulcanizates during exposure to sunlight and to outdoor weather for twelve months were studied. Figures 1, 1a, 2, 2a, and 3 show curves of the losses of tensile strength as a function of the time of exposure.

LATEX VULCANIZATES

Antioxygenic agents improve noticeably the maintenance of the mechanical properties during exposure. Vulcanizates containing PBN or DNPD lost about 40 per cent of their tensile strength by exposure to sunlight for twelve months, whereas the unprotected control vulcanizate lost more than 85 per cent (average of five samples) of its tensile strength during the same exposure. However, NBC in concentrations of 2-5 per cent reduced the loss of tensile strength to 18-30 per cent (see Figure 1). On the other hand, PBN was found to be superior as a protective agent against outdoor weathering, because vulcanizates containing it lost only 30 per cent of their tensile strength, compared with a loss of about 50 per cent for vulcanizates containing NBC. In each case the loss was much less than that of the unprotected control vulcanizate, which lost more than 80 per cent of its tensile strength (see Figure 2). In the case of latex vulcanizates, it is necessary to refer to the unprotected control vulcanizate to judge the improved resistance to exposure. As a matter of fact, protective agents in latex-rubber products have found little practical use, contrary to current practice with dry-rubber mixtures, where the use of PBN as a protective agent can still be regarded as the standard for judging protection against aging.

Combinations of NBC and protective agents, which have proved themselves to be disappointing as a means of protection against exposure cracking, seem, on the contrary, to be of value in preserving the mechanical properties of vulcanizates during exposure. An exception to this is the combination of PBN with NBC, which gives protection comparable to that imparted by NBC alone during exposure to sunlight (see Figure 1a). A combination of NBC and methyl di(*tert.*-butyl)phenol gives better protection, as far as mechanical properties are concerned, than does NBC alone on exposure to outdoor weather (see Figure 2a). The superiority of these combinations may depend on their capacity to increase the heat resistance of the vulcanizates.

A practical outcome of this work might be a study of the protection of latex-rubber vulcanizates against weathering by a combination of 1.5-2 per cent NBC and 0.5-1 per cent methyl di(*tert.*-butyl)phenol. Such combinations might retard the formation of cracks and, at the same time, aid in the maintenance of good mechanical properties during exposure.

Finally, oxidizability measurements, by the manometric method of Dufrasse, of vulcanizates exposed for twelve months to sunlight show the retard-

ing effect of NBC on the rate of absorption of oxygen, even after prolonged exposure (see Figure 5).

It should, however, be pointed out that the same measurements, made after exposure to outdoor weather, give a series of curves grouped much closer to the curve of the control unprotected vulcanizate.

VULCANIZATES OF DRY-RUBBER MIXTURES

A study of unloaded vulcanizates (of the composition already cited, with mercaptobenzothiazole as accelerator) showed little difference in their behavior on exposure to sunlight and to outdoor weather. This is contrary to what was found with the latex vulcanizates.

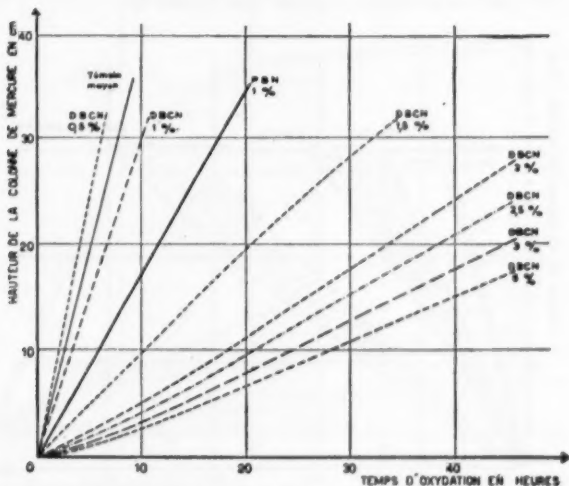


Fig. 5.—Latex-rubber vulcanizates. Oxidizability measurements, by the Dufraisse manometric method, of vulcanizates exposed 12 months to sunlight. The abscissa indicates the time of oxidation in hours; the ordinate the height (in cm.) of the mercury column of the manometer. The curve designated Témoin moyen is the unprotected control vulcanizate.

The most important result is the harmful effect of NBC alone. In less than ten months, vulcanizates containing NBC lost nearly all of their tensile strength, whereas the unprotected vulcanizate lost, in the same time of exposure, about 55 per cent, and vulcanizates containing PBN and DNPB, respectively, lost 20–25 per cent of their original tensile strengths (see Figure 3). Figure 3 shows also the beneficial effect of combinations of DNPB and PBN, and particularly of NBC and DPPD. The combination of NBC and DPPD, which resulted in a loss of only 20–25 per cent, is therefore remarkable in its effect on the maintenance of mechanical properties, while its superiority over PBN in its protection against sunlight cracking is great.

Experiments with vulcanizates reinforced with 10–50 per cent of carbon black (MPC) confirmed the superiority of NBC-DPPD combinations over any other system of protection studied. The protective action of NBC-DPPD combinations seems to be further enhanced by ZMBI. This study of rubber-carbon black vulcanizates is of particular interest because the most effective system of

protection, viz., NBC-DPPD, contains a compound that has a strong browning effect during exposure to sunlight, a fact which, of course, precludes its use in light colored vulcanizates. This problem will be dealt with in a separate publication.

Finally, there has been no detailed study of the correct proportions of protective agents to be used. In the present work, the attempt has been made to obtain, by the use of high proportions, to the greatest degree the specific effects desired. However, this aspect of the problem is of great importance, and the smallest proportions of NBC, DPPD, and ZMBI which give satisfactory protection in a practical way should by all means be investigated.

Oxidizability measurements after exposure of vulcanizates to outdoor weathering for one year confirm the excellent protection obtained with systems based on NBC and structuring agents (see Figure 6).

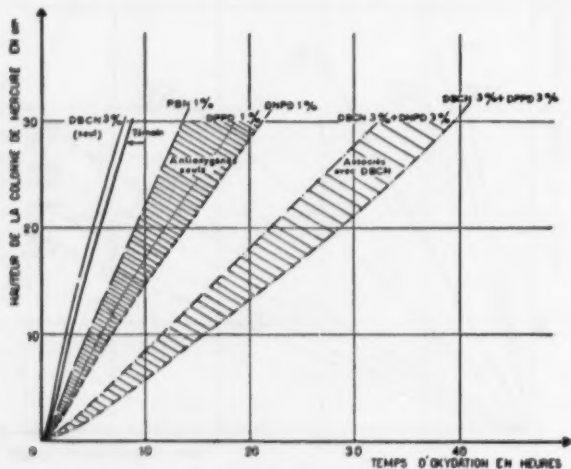


FIG. 6.—Dry-rubber vulcanizates containing no filler. Oxidizability measurements, by the Dufrasse manometric method, of vulcanizates exposed 12 months to outdoor weather. The abscissa indicates the time of oxidation in hours; the ordinate the height (in cm.) of the mercury column of the manometer. The left-hand curve is for the vulcanizate containing NBC alone. The next curve is for the unprotected vulcanizate. The left-hand cross-hatched area is for the antioxygenic agents alone; the right-hand cross-hatched area is for combinations of NBC and antioxygenic agents.

NATURAL AGING IN DARKNESS AND AT ORDINARY TEMPERATURE

In many cases, accelerated aging tests, e.g., the Geer oven, oxygen bomb, and manometric oxidizability measurements, are acceptable, in a first approximation, as satisfactory indications of the normal aging of vulcanized rubber when stored in darkness. As will be seen later, these tests gave in some cases perplexing results, so it was obviously necessary to confirm the results of the tests by a study of normal aging in darkness for twenty-four months. Aging for two years is admittedly an insufficient time to draw any formal conclusions, but it does give reliable indications of the aging characteristics of vulcanizates protected by NBC. Figure 7 shows the important results obtained.

The behavior of the unprotected vulcanizates should first of all be noted. The latex-rubber vulcanizate lost 15 per cent of its tensile strength; the dry-rubber vulcanizate only 6 per cent. Now it is generally accepted that latex-

rubber vulcanizates age better than do the corresponding dry-rubber vulcanizates¹⁵. This view seems to be based chiefly on aging tests by the oxygen-bomb method, which actually does indicate that unprotected latex-rubber vulcanizates age better and oxidize less rapidly (see Figure 8).

In the case of the latex-rubber vulcanizates containing from 1 to 5 per cent of NBC, the losses of tensile strength in two years were 7–12 per cent, compared with 15 per cent for the unprotected control vulcanizate. In the particular case studied, the antioxygenic agents gave values which differed insignificantly and ranged from 3 to 6 per cent (see Figure 7). These results are in accord with the oxidizability measurements (see Figure 8).

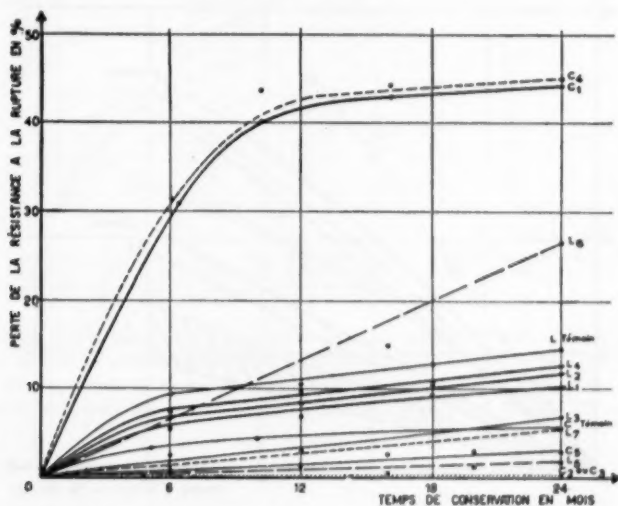


FIG. 7.—Latex-rubber vulcanizates (L) and dry-rubber vulcanizates (C). Loss of tensile strength as a function of the time of storage in darkness at 20° C. The curves designated *Témoin* are for the unprotected control vulcanizates.

L ₁ NBC 1%	C ₁ NBC 2%
L ₂ NBC 2%	C ₂ PBN 2%
L ₃ NBC 3%	C ₃ DNPD 2%
L ₄ NBC 5%	C ₄ NBC 3% + PBN 2%
L ₅ PBN 2%	C ₅ NBC 3% + DPPD 3%
L ₆ DNPD 2%	
L ₇ Methyl di(<i>tert.</i> -butyl)phenol 2%	

Dry-milled rubber was found to be extremely sensitive to the influence of NBC. In two years the losses of tensile strength reached the unusual value of 45 per cent, whereas the unprotected control vulcanizates lost only 6–7 per cent, and the vulcanizate containing PBN less than 1 per cent. The important result is the loss of 3 per cent by the vulcanizate containing a combination of NBC and DPPD, i.e., a loss only slightly greater than that of the vulcanizate containing PBN.

A means is, therefore, offered for obtaining very good natural aging by the use of a combination of NBC and DPPD, which is distinguished primarily for its protective action against cracking. Furthermore, oxidizability measurements made after latex-rubber and dry-rubber vulcanizates had been aged

naturally for twenty-four months' storage in darkness are in good accord with this conclusion (see Figure 8).

CORRELATION BETWEEN ACCELERATED AGING TESTS AND NATURAL AGING

Whenever, in the tests already described, a suitable protective system for the end in view was chosen, the natural aging tests indicate quite acceptable behavior from the practical standpoint, since nearly the same results were obtained as with standard protective agents, such as PBN. However, accelerated

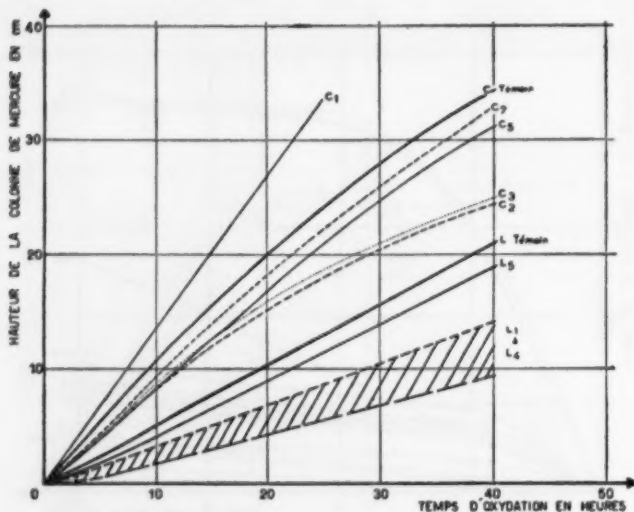


FIG. 8.—Latex-rubber vulcanizates (L) and dry-rubber vulcanizates (C). Oxidizability measurements, by the Dufraisse manometric method, of vulcanizates stored in darkness for 24 months at 20° C. The curves designated Témoin are for the unprotected control of vulcanizates.

L₁–L₆ NBC 1 to 5%
L₅ PBN 0.5 to 1%
C₁ NBC

C₃ PBN 2%
C₅ DPPD 2%
C₆ NBC 3% + DPPD 3%
C₇ NBC 3% + DNPD 3%

aging tests in the Geer oven and the oxygen bomb, made before these results were available, had given rather disturbing results in some cases.

LATEX VULCANIZATES

The losses of tensile strength during heat aging in a Geer oven at 70° C indicate that NBC has a definitely harmful effect, since the results place it in an unfavorable position with respect to the aging of the unprotected control vulcanizate (see Figure 9). Nevertheless, it should be noted that protective agents such as PBN, DNPD, and methyl di(*tert.*-butyl)phenol have almost as unfavorable an influence on aging as does NBC.

These results may seem rather surprising, but it should not be forgotten that latex-rubber vulcanizates often show an unexpected behavior, which is influenced by the particular accelerating system, the proportion of sulfur, the

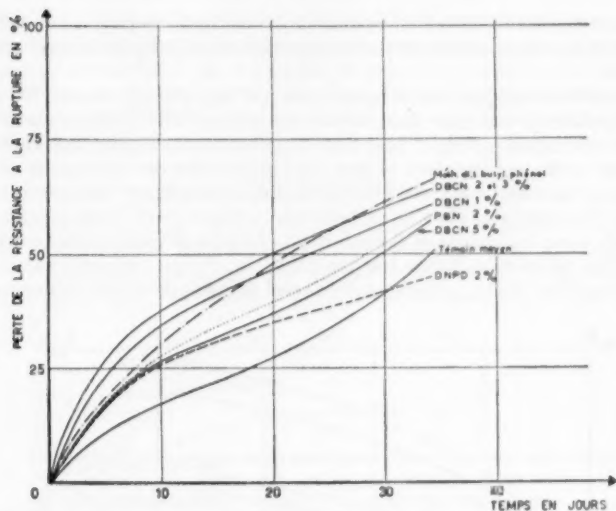


FIG. 9.—Latex-rubber vulcanizates. Loss of tensile strength by heating in an air oven at 70° C. The abscissa indicates the time in days; the ordinate the percentage loss of tensile strength. The curve designated Témoïn moyen is for the unprotected control vulcanizate.

processing conditions, etc. As Croux and Lemarchand have shown¹⁰, the protection of latex-rubber products always borders on the uncertain, and in many cases the protective agent actually has an unfavorable influence on aging. However this may be, it has been found that NBC (see Figure 9) has at least

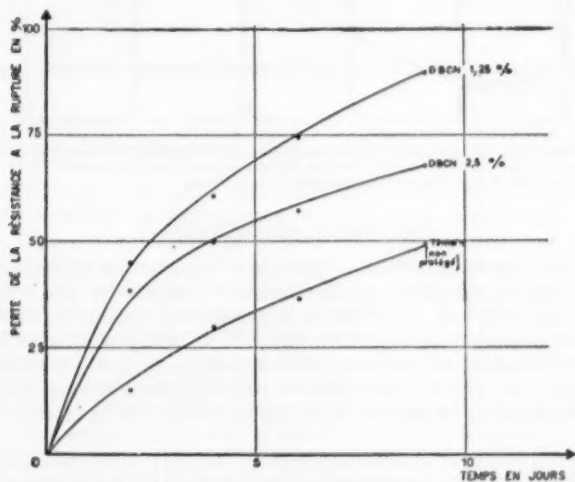


FIG. 10.—Latex-rubber vulcanizates. Loss of tensile strength by heating in oxygen under 20 kg. per sq. cm. pressure at 70° C. The abscissa indicates the time in days; the ordinate the percentage loss of tensile strength. The curve designated Témoïn is for the unprotected control vulcanizate.

a no greater unfavorable influence than PBN or than methyl di(*tert.*-butyl)-phenol in latex-rubber mixtures vulcanized with zinc diethyldithiocarbamate as accelerator.

The results of oxygen-bomb aging tests (20 kg. per sq. cm. at 70° C) are equally significant, and show that rubber containing NBC is particularly sensitive to the combined action of heat and oxygen under pressure (see Figure 10). This points to the evident lack of any correlation between the results of accelerated aging tests and natural aging in darkness at ordinary temperature. In this light, the results of Geer oven tests and oxygen-bomb tests should be regarded only as an indication of the sensitivity to heat of vulcanizates containing NBC. This, of course, limits the practical significance of accelerated aging tests as far as their being indicative of natural aging in darkness is concerned.

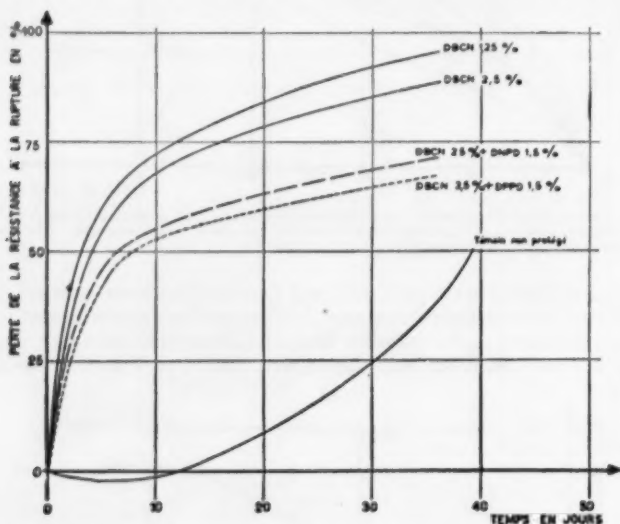


Fig. 11.—Dry-rubber vulcanizates. Loss of tensile strength by heating in an air oven at 70° C. The abscissa indicates the time in days; the ordinate the percentage loss of tensile strength. The curve designated *Témoins non protégés* is for the unprotected control vulcanizate.

DRY-RUBBER VULCANIZATES

To a greater degree even than in the case of latex-rubber vulcanizates, Geer oven and oxygen-bomb tests indicate that NBC has a very bad influence on aging (see Figures 11 and 12). This is in accord with the earlier experiments. Furthermore, a combination of NBC and DPPD, which is an excellent combination for protecting vulcanizates from loss of mechanical properties by exposure to light (see Figure 3) and also for retarding natural aging in darkness, has a deleterious effect on aging if judged by accelerated aging tests (see Figures 11 and 12).

The lack of any correlation between natural aging in darkness or on exposure to light and artificial accelerated aging tests is evident in this case too. The only possible information to be obtained from oxygen-bomb tests or Geer oven tests is the sensitivity to heat of vulcanizates containing NBC. The presence

of DPPD or, better still, a combination of DPPD and ZMBI, increases considerably the resistance to heat, without, however, giving as satisfactory results as might be wished for. In any event, recent experiments seem to indicate that the presence of certain reinforcing fillers impart to vulcanizates protected by NBC and DPPD satisfactory resistance to heat, without detracting from their other desirable characteristics.

CONCLUSIONS

Latex-rubber mixtures vulcanized with zinc diethyldithiocarbamate as accelerator show excellent resistance to sunlight if they contain 1.5–5 per cent of NBC. Combinations of protective agents which were tested contributed nothing to the protective effect of NBC alone as far as resistance to cracking is

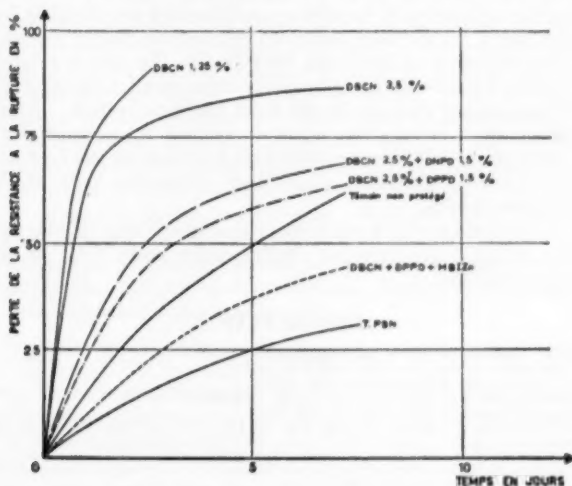


FIG. 12.—Dry-rubber mixtures. Loss of tensile strength by heating in oxygen under 20 kg. per sq. cm. pressure at 70° C. The abscissa indicates the time in days; the ordinate the percentage loss of tensile strength. The curve designated *Témoins non protégé* is for the unprotected control vulcanizate.

concerned; in fact, under some conditions they had an unfavorable influence. Only with respect to the maintenance of mechanical properties do these combinations have any noticeable protective effect, as do combinations of NBC with DNPB and with methyl di (*tert.*-butyl)phenol. However, such combinations should not be disregarded a priori, for it is possible that some of them would impart an appreciable increase of resistance to heat. In the present investigation, natural aging in darkness at ordinary temperature for twenty-four months was excellent, and this is at variance with the accelerated aging tests, except for the oxidizability measurements.

The behavior of dry-rubber vulcanizates accelerated by mercaptobenzo-thiazole differs greatly from that of corresponding latex-rubber vulcanizates. Only NBC showed any protective effect against cracking; on the contrary, it promoted a rapid loss of the mechanical properties of vulcanizates when they were exposed to light or were stored in darkness. The action of heat or oxygen under pressure is still more striking from this viewpoint. By the concurrent

action of structurizing agents, among which DPPD has been found to be the most effective, it is possible to attain a final protective effect which is manifest by a notable retardation of the appearance of cracks on exposure to light and by outdoor weathering, and at the same time, by a satisfactory retention of good mechanical properties during aging. Aging at ordinary temperature in darkness is likewise good, since the loss of tensile strength in two years was only 2-3 per cent. By way of comparison, a control vulcanizate, protected by PBN and stored under the same conditions, lost approximately 1 per cent of its tensile strength.

Recent experiments indicate that some carbon blacks have a very favorable effect. This should make it possible to utilize simultaneously effective protection against cracking, maintenance of good mechanical properties during exposure to light and during aging in darkness, and increased resistance to heat. This remarkable resistance to exposure cracking and to cracking by light of rubber-carbon black vulcanizates indicates the possibilities in the practical application of combinations of NBC and DPPD. In the case of reinforced mixtures, the combined effect of a complex nickel compound, a structurizing agent, and a deactivating agent seems to be the most effective system. The choice of the structurizing agent is very important, as are also the proportions of all the agents. A later study will be concerned with establishing the best proportions from the viewpoint of obtaining satisfactory protection with the minimum quantities of these agents.

Finally, it must always be kept in mind that there may be other protective agents which would make superior combinations with NBC or with other organic nickel complexes.

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CRYSTALLIZATION IN NATURAL RUBBER

II. THE INFLUENCE OF IMPURITIES *

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INTRODUCTION

In a previous publication¹, the factors affecting the rate of crystallization in natural-rubber vulcanizates have been examined. In the course of an experimental study of the influence of various chemical modifications on the rate of crystallization of natural rubber, the rates of crystallization of different types of raw rubber at the temperature of -26°C were found to be markedly dissimilar. Such differences have previously been noticed², although their origin has been obscure. Measurements of the rate of crystallization are described below, and evidence is given for ascribing the differences in rates to the influence of some of the non-rubber components. The well known effect of foreign particles in stimulating the crystallization of supercooled liquids may be considered as analogous, and similar effects have been anticipated hypothetically³ in the crystallization of long chain polymers. However, no previous experimental evidence appears to have been adduced.

EXPERIMENTAL

The progress of crystallization in various samples of raw rubber was followed dilatometrically⁴, using mercury as the confining liquid. The test-piece, in the form of a rod of approximately 100 mm. length and square cross-section of about 4 mm. side, was wrapped in stainless steel woven gauze (41 gauge, 100 mesh), before being sealed into the bulb of the glass dilatometer, in order to restrain the rubber from flowing under the conditioning treatment adopted. This consisted of heating the sealed dilatometer, after filling with mercury, for a period of about 1 hour at a temperature of 100°C . It was then left at 21°C for about 16 hours before being placed in an alcohol bath in a refrigerated chamber at a temperature of -26°C . After a large initial thermal contraction which was substantially complete in 5 minutes, slow further changes in volume took place which are attributed to crystallization of the rubber. If the conditioning period at 100°C was omitted, the progress of crystallization at -26°C was found to be variable and to be governed by time functions of the forms previously shown¹ to characterize the crystallization of vulcanized rubber stretched to various extents. This behavior is ascribed to residual orientation in the test-piece probably occurring in preparation. The conditioning period at 100°C proved adequate to enable reproducible measurements to be obtained, and the corresponding time functions were found to be of the forms to be anticipated in unstrained rubber. The complete omission of the period of standing at 21°C

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was found to affect the crystallization process to a secondary extent only. Large reductions of the molecular weight produced by heavy mastication on an open mill were also found to have only secondary effects on the rate of crystallization for the various raw rubbers examined.

No true equilibrium decrease of volume was attained during the course of observations, since after the large primary crystallization, further protracted small decreases of volume were observed.

RESULTS

The rate of crystallization may be characterized by the time at which half the quasi-equilibrium decrease of volume occurs, since the volume alters rapidly

TABLE 1

Rubber sample	Half-life of crystallization at -26°C (min.)
Skim crepe	110
Smoked sheet I	123
Pale crepe	126
Smoked sheet II (Wood and Bekkedahl) ⁴	144
Pale crepe, after extraction with acetone	410
Smoked sheet I, after extraction with acetone	450
Deproteinized crepe, after extraction with acetone	470
Deproteinized crepe	475

with time at this stage, and errors in the estimate of the final decrease of volume do not give rise to comparable errors in the half-life. In Table 1, the half-lives of the crystallization process at -26°C are given for the various raw rubbers examined, together with the value obtained by Wood and Bekkedahl⁴ for their sample of smoked-sheet rubber.

The results are seen to fall broadly into two classes; about 120 and about 450 minutes, with the rubbers containing generally higher amounts of nonrubber

TABLE 2

Substance added to extracted smoked sheet I	Amount (% by weight)	Half-life of crystallization at -26°C (min.)
Stearic acid	0.1	182
Stearic acid	1	115
Stearic acid	4	102
Zinc stearate	2	112
Paraffin wax	2	150
Oleic acid	2	180
Zinc oxide	2	500
Carbon black (MPC black)	2	550
L-Arginine	1	500

components exhibiting more rapid crystallization. In a second series of experiments, the results of which are presented in Table 2, small amounts of foreign substances were incorporated on an open mill into a sample of smoked-sheet rubber which had been previously extracted with acetone. Some of the substances chosen are representative of the materials found to be present⁸ in smoked sheet, while others are added to rubber in conventional manufacturing processes. Small amounts of those substances which have relatively long molecules and also crystallize readily are seen to increase the rate of crystalliza-

tion of the extracted rubber towards that found for the unextracted sample. Stearic acid is particularly effective in this respect.

In Figure 1, the decrease of volume is plotted against time at a temperature of -26°C for the unextracted and extracted samples of smoked sheet and for the sample of extracted smoked sheet to which 1 per cent of stearic acid had been added. The full curves of Figure 1 are of the form:

$$-\Delta v/v = A[1 - \exp(-kt^2)]$$

which has been shown⁶ to arise from the growth of spherical crystals at a constant radial rate from nuclei which are all existent at an early stage, no appreci-

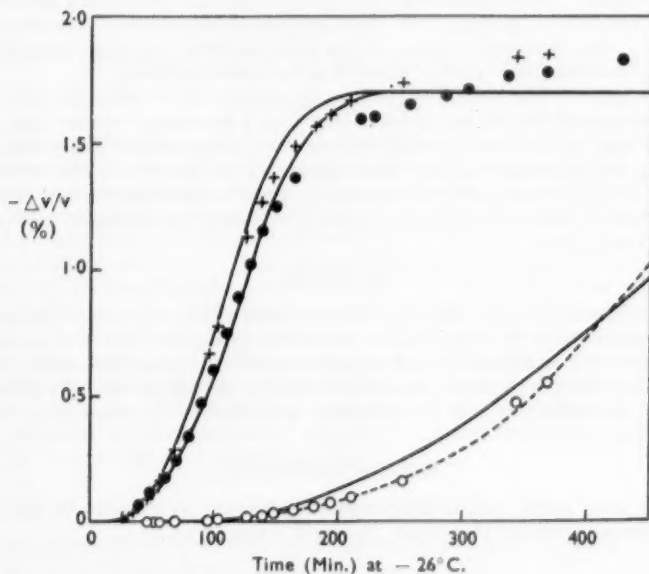


FIG. 1.—The progress of crystallization in raw rubber. Smoked sheet ●, smoked sheet after extraction with acetone ○, acetone-extracted smoked sheet with 1 per cent of stearic acid added +. The full curves are of the form: $-\Delta s/v = A[1 - \exp(-kt^2)]$. The broken curve is of the form: $-\Delta s/v = A[1 - \exp(-kt^4)]$.

able additional ones being formed as crystallization proceeds. The numerical parameters were chosen to provide the best fit with the experimental points, and the consequent agreement is satisfactory to a first approximation for the rapidly crystallizing samples. However, for the slowly crystallizing sample, the agreement in the early stages is markedly improved when a time function of the form:

$$-\Delta v/v = A[1 - \exp(-kt^4)]$$

is taken; the broken curve of Figure 1 being of this form. Such a time function has been shown⁶ to arise from the growth of spherical crystals from nuclei which appear at a constant rate in time and grow at a constant radial velocity.

CONCLUSIONS

It appears that various types of plantation rubber contain among their non-rubber components substances which effectively promote the crystallization process under the conditions described. In particular, the sample of rubber which was used in the experimental work of Wood and Bekkedahl⁴ on the temperature dependence of the crystallization rate apparently contained such active material. It has been shown that extraction with acetone removes the relevant impurities, and the time function governing the progress of crystallization in extracted samples suggests that nucleation there occurs sporadically. This is the behavior to be anticipated for the pure polymer and the removal of the residual impurities from the extracted sample may be expected to have little further effect. It is possible that the crystal habit may be altered in the presence of suitable impurities, with corresponding changes of the rate of crystallization. The observed changes of the time function, however, suggest that nucleus formation is primarily affected in the cases examined.

Schallamach⁷ has identified the long spacing in rubber with the nonrubber components and has shown, in particular, that 2 per cent of stearic acid incorporated into purified rubber reintroduces the long spacing. The existence of the long spacing suggests that these impurities are present in the crystalline form in rubber at ambient temperatures. Such a condition for the impurity at the temperature of crystallization seems necessary for successful catalysis of crystal nucleation.

SUMMARY

Experiments are described in which the effect of the presence of foreign substances on the rate of crystallization of natural rubber at -26°C is examined. It is shown that small amounts of suitable impurities, some of which are present in smoked sheet and other plantation rubbers, accelerate the crystallization process markedly at this temperature, presumably by promoting crystal nucleation.

ACKNOWLEDGMENT

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III. FILLED COMPOUNDS

INTRODUCTION

The crystallization of well vulcanized natural rubber compounds is generally sufficiently slow to be ignored in applications where the rubber component is subjected to relatively small strains¹. When a considerable degree of strain is applied, however, and the strained component is subjected to low temperatures

for long periods, the occurrence of crystallization and the consequent hardening and relaxation of stress may present serious practical problems. In an earlier publication², factors affecting the rate of crystallization and the corresponding relaxation of stress in stretched natural rubber vulcanizates have been examined, and in another previous work³ the influence of suitable impurities, notably stearic acid, in promoting the crystallization process in raw rubber has been described. The purpose of the present study has been to investigate the effect of the presence of large quantities of fillers on the rate and extent of crystallization in natural rubber subjected to simple extension in the range of extension ratio 1 to 3. The observations of stress and volume changes were carried out at a temperature of -26°C , because the rate of crystallization has previously been found to be a maximum at this temperature for unvulcanized and vulcanized natural rubber⁴.

CRYSTALLIZATION IN THE UNSTRAINED STATE

EXPERIMENTAL METHOD

The crystallization of unstretched unvulcanized samples was followed with time at a temperature of -26°C , using a dilatometric technique⁵ for observing the corresponding volume changes. Test-pieces were prepared by molding for 15 minutes at a temperature of 140°C from smoked-sheet rubber to which 50 parts by weight of HAF black had been added on an open mill and from the rubber without additives. The heating period proved adequate to yield test-pieces which were effectively unoriented, and also simulated normal vulcanization conditions. The test-pieces were 10 cm. long and of rectangular cross-section, 4 mm. and 5 mm. They were sealed into the bulbs of glass dilatometers, which were subsequently filled with mercury. The dilatometers were then placed in a tank of alcohol in a refrigerated chamber at a temperature of -26°C . A large initial thermal contraction occurred, which was complete in about 10 minutes, after which further slow changes of volume took place. These are ascribed to crystallization of the rubber.

EXPERIMENTAL RESULTS

The experimental observations are presented in Figure 1. The full curves of Figure 1 are of the form:

$$-\Delta v/v = A(1 - \exp(-kt^2))$$

shown previously² to represent to a first approximation the crystallization process at this temperature in unstrained vulcanized natural rubber. Such a time function would arise from the growth of spherical crystals at a constant radial rate, from nuclei which are all present initially. The numerical parameters A , k were chosen to give the best agreement with the experimental points.

No true equilibrium decrease of volume was attained during the course of observations, and estimates of the final decrease of volume are, therefore, necessarily approximate. The rate of crystallization may be characterized more precisely, however, by the time at which half of the quasi-equilibrium decrease of volume occurs, as described earlier².

The half-lives and final volume changes are given in Table 1. It is seen that the crystallization process is somewhat more protracted for the rubber containing carbon black, though the extent of the retardation is slight compared for example with that occasioned by the introduction of a relatively small num-

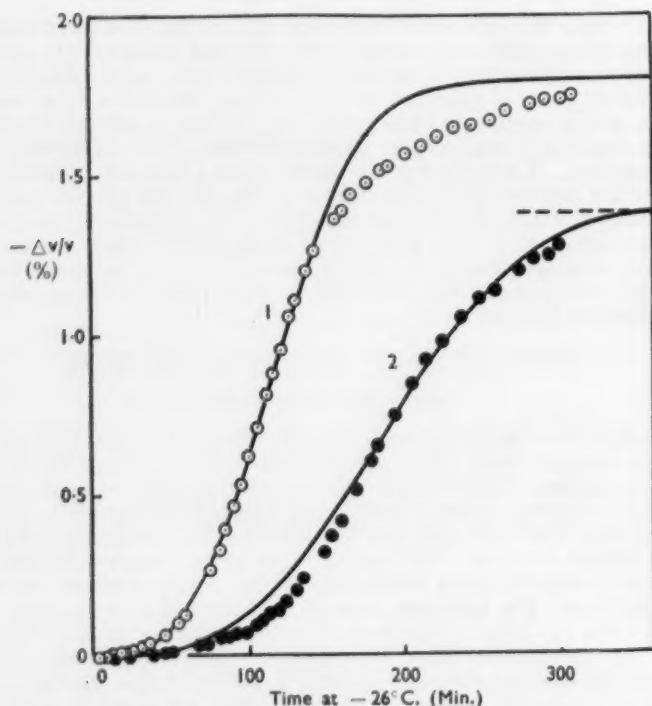


FIG. 1.—Changes of volume with time at -26°C for smoked sheet, 1, and smoked sheet containing 50 parts of HAF black, 2.

ber of cross-links². It was found, in a subsidiary experiment, that severe mastication of smoked-sheet rubber on an open mill did not greatly influence the rate of crystallization. It may be assumed, therefore, that the breakdown of the rubber which occurred when the carbon black was added was without effect, and the slight retardation of crystallization may reasonably be ascribed to the reduction of the mobility of chain segments occasioned by the presence of large quantities of small particles.

The reinforcing carbon blacks have been found⁶ to impair the cross-linking

TABLE 1

Test-piece	Observed volume change (%)	Half-life (min. at -26°C)	Volume fraction of rubber in test-piece	Volume change (% of rubber content)
Smoked sheet	1.80	117	1.0	1.80
Smoked sheet + 50 parts by weight HAF black	1.38	185	0.79	1.75
Vulcanizate A (unfilled)	1.60	2800	1.0	1.60
Vulcanizate B (50 parts by weight of lampblack)	1.28	2100	0.79	1.63
Vulcanizate C (50 parts by weight of HAF black)	1.28	1850	0.79	1.63

action of convenient peroxide vulcanizing agents, presumably by causing decomposition of the peroxide, and it was not, therefore, practicable to study the crystallization of such simple vulcanizates containing carbon black. It seemed desirable, however, to choose a vulcanization system in which the amount of sulfur combined in forms other than cross-links was relatively low in order that the crystallization process should not be unduly prolonged². Test-pieces were, therefore, prepared from the mix formulations and vulcanization conditions given in the Appendix, and the progress of crystallization at -26°C was followed by observations of the accompanying volume changes. The experimentally observed half-lives of the crystallization process for these vulcanizates are

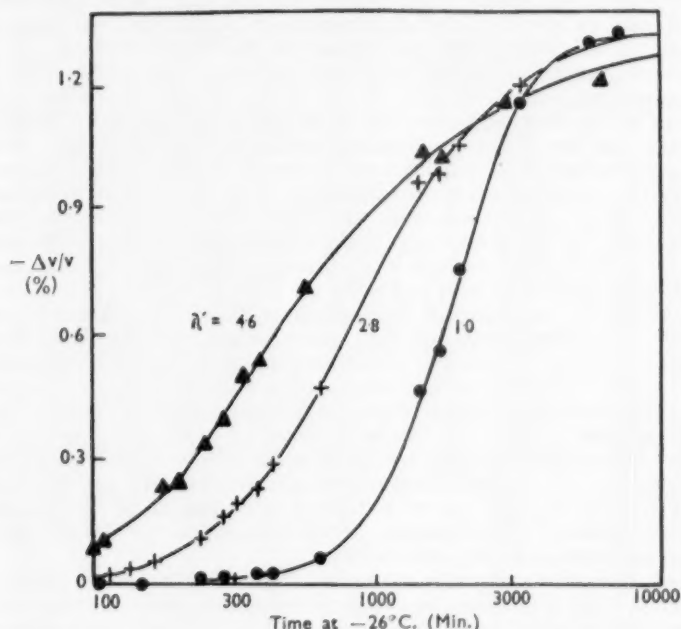


Fig. 2.—Changes of volume with time at -26°C for vulcanizate C after extending to various values of extension ratio, λ' , and releasing, prior to test.

given in Table 1, together with the final volume changes. The crystallization process is seen to be many times slower in the vulcanized rubbers.

The vulcanizates containing carbon black crystallized somewhat more quickly than the unfilled vulcanizate, and this may be attributed to a reduction of the degree of cross-linking of these test-pieces, in comparison with that prepared from the unfilled compound, possibly caused by some absorption of the vulcanizing agent by the carbon blacks. However, the rate of crystallization is again seen to be unaffected to a first approximation by the presence of large quantities of carbon black. Moreover, on presenting the experimentally observed quasi-equilibrium decrease in volume as a fraction of the rubber component present, it was found that the extent of crystallization is similarly unaffected by the presence of carbon black, as shown in Table 1. It appears,

therefore, that the carbon black does not immobilize large quantities of rubber in such a manner as to prevent their crystallization, and the reduction of mobility of chain segments occasioned by the presence of carbon black may be considered small.

Measurements of the volume change consequent on crystallization were also made, using test-pieces of the filled vulcanizate, after previously stretching them in simple extension to extension ratios of approximately 2.8 and 4.6 for 1 minute and then releasing them. The residual extensions exhibited by the HAF black-filled vulcanizate were 7 and 15 per cent of the original length, respectively. The resulting curves of volume change with time at a temperature of -26°C are shown in Figure 2 for the HAF black-filled vulcanizate, together with the curve obtained on the test-piece which had not been previously strained. Similar results were also obtained for the lampblack-filled vulcanizate. Some acceleration of the crystallization process was produced by the prior extension, as shown in Figure 2, and this may partly be ascribed to the breakage of attachments between the carbon-black particles and the rubber molecules, and the consequent enhanced mobility of chain segments. Moreover, if such an enhanced mobility were restricted to specific plane sections, as is implicit in the theoretical model proposed by Mullins and Tobin⁷ to represent the softening of carbon black-filled vulcanizates by prior extension, the somewhat more diffuse time-dependence of the crystallization process in the previously extended test-pieces might be reasonably attributed to the more rapid growth of the crystals in these directions.

However, the acceleration of the crystallization process produced by prior extension is considerably greater than would be expected from a partial recovery of mobility. In the previous section, where the rate of crystallization of raw rubber containing an equivalent carbon-black content was compared with that of the original smoked sheet, the half-life of the crystallization process for the filled rubber was shown to be greater by a factor of somewhat less than 2. It is unlikely that the restraining effect of the carbon-black particles on the mobility of the crystallizing rubber units is completely removed by the prior extensions imposed, yet the half-life of crystallization for the test-piece previously stretched to an extension ratio of 4.6 is less than one-third that for the test-piece not previously stretched.

It seems probable, therefore, that some elements of the rubber matrix are retained in a highly strained state relative to the whole when the test-piece is relaxed after being subjected to a large extension. Crystal nucleation and growth will then occur rapidly in these regions and promote the crystallization of the bulk.

STRESS RELAXATION IN STRETCHED VULCANIZATES

EXPERIMENTAL METHOD

The relaxation of stress consequent on crystallization in stretched test-pieces was followed experimentally as described below. The test-pieces were prepared from the mix formulations and vulcanization conditions given in the Appendix as molded rods of rectangular cross-section of sides 4 mm. and 5 mm., over a central region 10 cm. long. They had large square ends of similar thickness, by means of which they could be held in two metal clamps, the lower one being fixed to a light metal frame, while the upper one rested on two of a series of fixed metal pins projecting from the frame and so positioned that the central region of the test-piece was extended by various known amounts.

In order to measure the tensile stress remaining in the test-piece after intervals of time at a temperature of -26°C , the frame carrying the extended test-piece was placed in a large vacuum flask before being removed from the refrigerated chamber and attached to the stress-measuring apparatus shown in Figure 3a. This comprised a steel helical spring, the lower end of which was

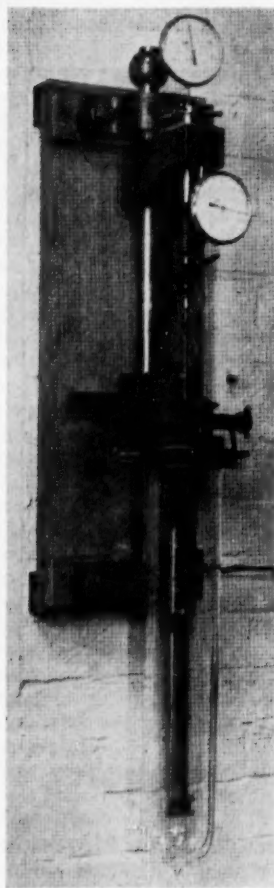


Fig. 3a.—Stress measuring apparatus.

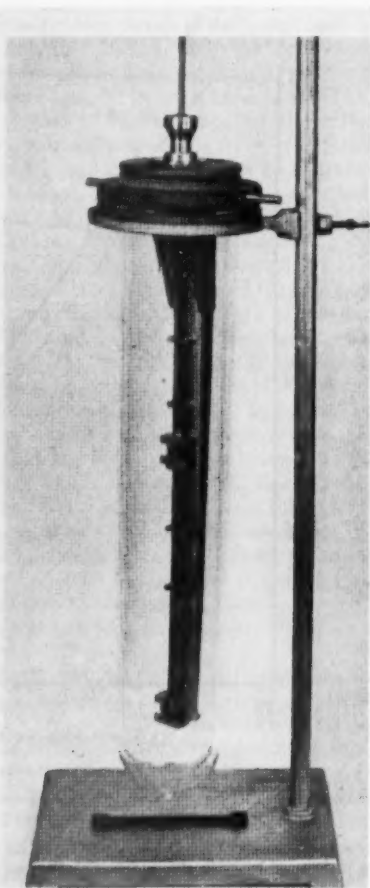


Fig. 3b.—Frame holding stretched test-piece.

connected to the upper test-piece clamp through a small hole in the Tufnol lid of the vacuum flask, while the upper end was capable of being raised by rotating a capstan nut. The movements of the ends of the spring were measured with the aid of two dial gauges, enabling the spring deflection to be determined. The movement of the clamp holding the upper end of the test-piece clear of its supporting pins was detected by the resulting break in an electric circuit containing a signal lamp, and the spring deflection at that instant provided a meas-

ure of the tensile stress remaining in the test-piece. The measurement of stress is readily completed in 1 minute, while the vacuum flask was found to retain the sample and frame at the temperature of the refrigerated chamber for much longer periods. On completing the measurement, the frame was returned to the refrigerated chamber and there withdrawn from the vacuum flask, which was thus available for use with several frames. In Figure 3b, a frame carrying a stretched test-piece is shown inside the vacuum flask, as withdrawn from the

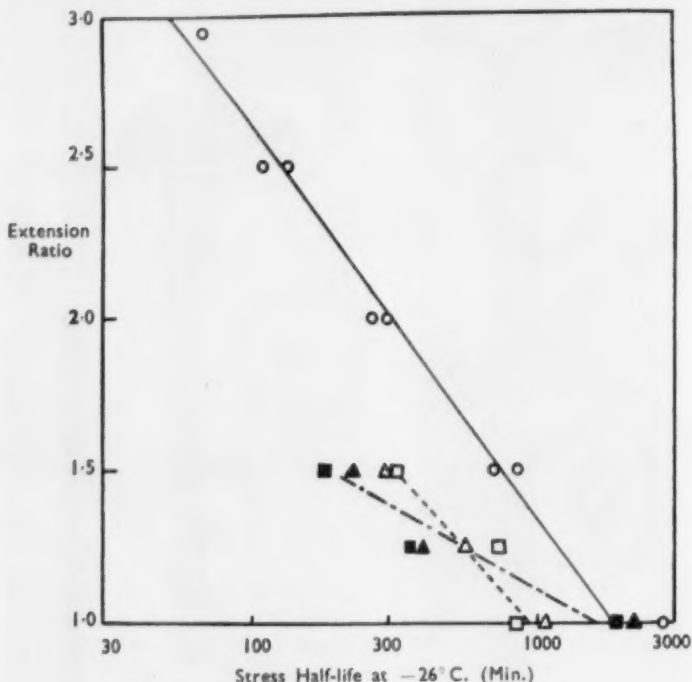


FIG. 4.—Variation of stress half-life with extension ratio for vulcanizate A, \circ ; vulcanizate B, \blacktriangle ; vulcanizate C, \blacksquare . Experimental points obtained after extending to an extension ratio of approximately 2.8, and releasing, prior to test: vulcanizate B, \triangle ; vulcanizate C, \square .

refrigerated chamber together with an unextended test-piece. In practice the glass vacuum flask is covered with a protective shield in case of fracture.

EXPERIMENTAL RESULTS

Measurements of the tensile stress after intervals of time at -26°C were made for test-pieces of the unfilled vulcanizate subjected to simple extension in the range of extension ratio 1.5 to 3.0. In all cases, the tensile stress was observed to relax to zero, after which a pronounced subsequent extension occurred. The times at which the stress was reduced to one half of the original value may be used to characterize the rate of relaxation of stress, and in Figure 4 the stress half-lives are plotted against the extension ratio imposed, the experi-

mental points for the unfilled vulcanizate here considered being represented by open circles. A linear relation is seen to obtain, as reported previously³ for similar materials, extrapolating to give approximate agreement with the half-life of crystallization, determined dilatometrically for the unstrained vulcanizate, denoted by an open circle on the abscissa.

Similar measurements of the relaxation of stress in the lampblack and HAF black-filled vulcanizates were made at extension ratios of 1.25 and 1.50. The initial stresses were, of course, considerably higher than the corresponding stresses in the unfilled vulcanizate, but relaxed in a similar manner to zero in all cases, small subsequent extensions being observed in some instances. The corresponding stress half-lives are also plotted in Figure 4 against the extension ratio imposed, together with the previously determined half-life of crystallization in the unstretched state. While a linear relation is seen to characterize these results approximately, it is of a much reduced inclination, so that the stress half-life at 50 per cent extension is comparable with that exhibited by the unfilled vulcanizate at about 125 per cent extension. This is in accord with the proposed theoretical model⁷ for filled rubbers, where a given overall extension is considered to comprise considerably higher local extensions of elements of the rubber matrix which are freed from immobilizing attachments to the carbon particles. It has also been proposed⁷ that such freed elements are augmented by prestraining to a higher extension ratio. The imposition of a given overall extension therefore involves lower effective extensions of elements of the rubber matrix after a large prior strain. When measurements of the half-life of stress relaxation were made for extended test-pieces which had been prestrained to higher extension ratios, it was found that the half-lives were increased by prestraining to extension ratios in the range 2 to 3, in accord with this hypothesis. It has already been observed that the half-life of crystallization in the unstrained state is reduced by prior extension. The experimental measurements of the half-lives of stress relaxation and crystallization after prestraining to an extension ratio of 2:8 are plotted in Figure 4 as open squares and triangles, and the slope of the approximately linear relation characterizing them is seen to be greater as a result of the prestraining treatment, and comparable with that obtained for the unfilled vulcanizate.

Measurements were made of the relaxation of stress for the filled vulcanizates subjected to rather higher extensions of extension ratios 2 and 2.5. In these cases a protracted relaxation occurred which was diffuse in time and incapable of representation by an equation of the simple form shown previously to characterize the crystallization of rubber from the amorphous state. Similar behavior is exhibited by unfilled vulcanizates extended to extension ratios exceeding about 4, and is ascribed to the existence of a crystalline structure occasioned by the extension at room temperature which obstructs the attainment of an equilibrium degree of crystallization when the test-piece is placed at a temperature of -26°C . This behavior in the filled vulcanizates at much lower extension ratios is also in accord with the hypothesis that elements of the rubber network are subjected to extensions considerably higher than the imposed overall extension.

OTHER FILLERS

Observations of the relaxation of stress at a temperature of -26°C were made for vulcanizates containing colloidal china clay. The stress relaxation behavior was generally similar to that observed for the corresponding unfilled vulcanizate.

The stress relaxation was also determined for vulcanizates of rubber containing polymethyl methacrylate either in the form of an intimate mixture or chemically combined to the rubber molecules⁸, and of rubber containing cyclized rubber⁹, as the reinforcing ingredients. The behavior was again found to be similar to that observed for the unfilled vulcanizate. Experimental measurements of the volume changes accompanying crystallization in the unstrained unvulcanized materials also indicated that these polymeric stiffening agents did not appreciably influence the progress of crystallization. Some influence of chemically combined polymeric stiffening agents might have been expected in view of the previously reported¹⁰ influence of cross-links and combined sulfur on the rate of crystallization. The calculation of the number of sites at which a chemical attachment to the rubber molecule has been effected is, however, rendered inaccurate in the present case by the uncertainty in determining¹¹ the length of such short attached chains (between 1000 and 10,000 molecular weight units).

GENERAL CONCLUSIONS

Experimental measurements have been described of the relaxation of stress in stretched filled rubbers and of the changes of volume of the unstretched materials, associated with crystallization at a temperature of -26°C . It appears that the presence of large quantities of particle and polymeric fillers does not significantly impede the progress of crystallization in the rubber component in the unstrained state, while certain structure effects associated with the prior extension of carbon black-filled vulcanizates may considerably accelerate it. This acceleration is attributed in part to the existence of oriented regions in the rubber matrix of a carbon black-filled vulcanizate after a prior large extension. The pronounced anisotropy to tearing exhibited by a previously extended carbon black-filled vulcanizate may also be considered evidence for such residual orientation.

Stress relaxation was found to proceed readily in stretched filled vulcanizates, complete relaxation being observed at extension ratios of 1.25 and 1.5. Moreover, the rate of relaxation of stress is considerably greater than for the unfilled vulcanizate at these extensions, in accord with the theoretical model proposed⁷ for filled vulcanizates. Though a prior large extension reduced the difference between the rates of stress relaxation of the filled and unfilled vulcanizates at extension ratios of 1.25 and 1.5, in agreement with the theoretical model, the effect was to some extent compensated, presumably by the accelerating influence of the residual oriented regions produced by the prestraining treatment.

It seems clear, therefore, that the incorporation of fillers affords no protection against the crystallization of rubber components held for long periods at low temperatures; indeed, the presence of suitable quantities of carbon black may cause some acceleration of the process in components subjected to moderate strains.

SUMMARY

Measurements are described of the changes of volume accompanying crystallization in filled vulcanized natural rubber, and of the corresponding relaxation of stress in extended test-pieces. The observed changes in the rate of crystallization and relaxation of stress are attributed to the reduction in mobility of the rubber molecules in the neighborhood of foreign particles and to the

effective higher orientation of some elements of the rubber matrix when the filled vulcanizate is subjected to simple extension.

ACKNOWLEDGMENTS

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APPENDIX

The following mix formulations and vulcanization conditions were used for the preparation of test-pieces:

	A	B	C
Smoked sheet (parts by weight)	100	100	100
Zinc oxide (parts by weight)	5	5	5
Stearic acid (parts by weight)	2	2	2
Tetramethylthiuram disulfide (parts by weight)	4	4	4
Lampblack (parts by weight)	—	50	—
HAF black (Philblack-O) (parts by weight)	—	—	50

Vulcanization was 45 minutes at 140° C.

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THE INTERACTION OF SULFUR AND SULFUR
COMPOUNDS WITH OLEFINIC SUBSTANCES.
VII. LOW-TEMPERATURE SULFURATION OF
TRIALKYLETHYLENES WITH HYDROGEN
SULFIDE-SULFUR DIOXIDE AND WITH A
SULFUR-ZINC DITHIOCARBAMATE
SYSTEM *

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INTRODUCTION

Previous investigations¹ of the interaction of olefins with sulfur at about 140° C, undertaken to gain an insight into the mechanism of rubber-sulfur vulcanization, have revealed that the products result from a complex series of processes. It is, therefore, important to study comparable reactions under the mildest possible conditions in the hope of determining the primary sulfuration process, and the work now reported sought to achieve this purpose by employing sulfuration procedures known to effect vulcanization at room temperature. The two procedures used were: (1) Peachey's process², involving the alternate treatment of the olefin with sulfur dioxide and hydrogen sulfide at 0°; (2) sulfuration of the olefin with sulfur at room temperature in the presence of hydrogen sulfide, zinc oxide and zinc dibutyldithiocarbamate, the last substance typifying the ultra-accelerators used in low-temperature vulcanization.

SULFURATION WITH HYDROGEN SULFIDE-SULFUR DIOXIDE

A number of olefins were treated by this method to determine the influence of (1) the unsaturation pattern and (2) alkyl substitution at the α -methylene carbon atom on the ease of sulfuration. The former factor was found to exert a critical influence, the latter to be comparatively unimportant. Trialkyl substitution at the double bond appeared to be necessary for reactivity, and the major sulfurated products isolated were invariably substances that from elementary analyses and infrared spectroscopic characteristics were identified as *dialkenyl tetrasulfides*, $(R_2C:CH \cdot CHR \cdot S \cdot S)_2$. The terpenoid olefins 2,6-dimethylocta-2,6-diene and squalene reacted analogously to the monoolefins studied, and, in contrast with the sulfuration of these olefins with sulfur at 140° C³, yielded no cyclic sulfide derivatives. The infrared spectroscopic data showed that the original $R_2C:CHR$ type of unsaturation was largely retained, but that other types of unsaturation arising from double-bond rearrangement were present to a minor extent. Hydrogenolysis of the tetrasulfide from 2,4-

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dimethylpent-2-ene with lithium aluminum hydride yielded dimethylpentene-thiol, as is consistent with the dialkenyl constitution of the reactant. Similar hydrogenolysis of the product from squalene results in the removal of approximately half of the combined sulfur, in keeping with its tetrasulfidic nature. Oxygenated sulfur compounds comprised minor products of the Peachey sulfuration; they were formed possibly by the action of polythionic acids on the olefin.

The two distinctive features of the Peachey cross-linking process are, therefore, (1) its wholly substitutive character and (2) the practically exclusive formation of S_4 cross-links. Considerable speculation has been directed towards identifying the nature of the nascent sulfur deposited on mixing hydrogen sulfide and sulfur dioxide in the presence of moisture. Thus, Bedford & Sebrell⁴ argued that the active sulfur is trithiozone, S_3 , although more recent knowledge casts increasing doubt on the possible existence of this substance. On the other hand, the existence of S_2 molecules⁵ or diradicals⁶ in sulfur vapor above 500°C is well recognized. The most reasonable interpretation of the reaction course is that S_2 units, derived from the prior reaction of hydrogen sulfide and sulfur dioxide, are substituted at the α -methylene carbon atom—probably via substituted allyl radicals, since double-bond displacements occur—and that the reaction conditions then lead almost entirely to self-coupling of the alkenyldithio radicals, $R_2C:CH\cdot CHR\cdot S\cdot S\cdot$. The coupling of alkenylthio ($R\cdot S\cdot$) radicals or thiols, or possibly of hydropolysulfides, cannot be excluded, however, since it has been found that butane- and toluene- ω -thiols, when caused to react similarly with hydrogen sulfide-sulfur dioxide, also yield the respective tetrasulfides.

The dialkenyl tetrasulfide nature of the products obtained by the present procedure is in marked contrast with the alkyl alkenyl polysulfide nature of the products formed in the olefin-sulfur reaction at elevated temperatures¹. It might be assumed that the primary sulfuration products in both cases are dialkenyl polysulfides, and that, at the higher temperature, these are thermally unstable and decompose to give alkenylthio radicals that react additively with the parent olefin to give the observed products. There is apparent support for this assumption in that the reaction of 2,4-dimethylpent-2-ene with hydrogen sulfide-sulfur dioxide at 83°C yields a mixture of tri- and tetrasulfides, whose analyses and spectroscopic characteristics correspond to an alkyl alkenyl structure. Nevertheless, when dialkenyl tetrasulfides were heated with the corresponding olefin at 83° or 140°C , little reaction was evident, and significantly, for the dialkenyl tetrasulfide derived from 2,6-dimethylocta-2,6-diene, only a trace of the characteristic cyclic monosulfide was formed. These findings form a marked contrast with previous observations⁷, on the decomposition of other types of polysulfides. The apparent thermal stability of the dialkenyl tetrasulfides is clearly inconsistent with the above-mentioned assumption about the source of alkyl alkenyl structures, and indicates that some intrinsic feature of the primary sulfuration reaction at the higher temperatures is responsible for the appearance of alkyl units.

SULFURATION INDUCED BY ZINC DIBUTYLDITHIOCARBAMATE

Treatment of the olefin ($R_2C:CHR$) with sulfur, zinc oxide, and zinc dibutyldithiocarbamate at room temperature in the presence or absence of a trace of hydrogen sulfide yielded a product which, when subjected to chromatographic fractionation, gave a small yield of olefin polysulfide containing a little

free sulfur. These polysulfides gave analytical figures and possessed the spectroscopic features appropriate to dialkenyl tetrasulfides, although a tendency for higher-polysulfide formation, probably attributable to dissolved free sulfur, is apparent. These products bore a close resemblance to those obtained by procedure (1), and such similarity was reflected in the occurrence of double-bond displacements to a minor extent and the absence of cyclic sulfide when 2,6-dimethylocta-2,6-diene was employed.

Two notable features of this sulfuration procedure are (1) the large discrepancy between the amount of olefin taking part in the reaction and the amount (about one-third) that is found in the polysulfide, and (2) the catalytic influence of hydrogen sulfide.

(1) The olefin unaccounted for is presumably combined in the more strongly absorbed materials, containing nitrogen and sulfur, encountered in the separation procedure, and indicates the occurrence of important alternative or secondary reactions other than the simple linking of olefin molecules by sulfur chains. The experiments on the tetrasulfide stability referred to above imply that these unknown reactions do not involve previously formed tetrasulfide (unless the accelerator system potentially promotes its breakdown), and it would seem that the intermediates react in no single manner, but engage in competitive stabilizing processes. There is no evidence as to whether these processes involve the linking of two or more olefin molecules and thus constitute an additional mode of cross-linking.

(2) It was found that 1-methylcyclohexene undergoes sulfuration at room temperature in the absence of hydrogen sulfide, but that the other trialkylethylenes examined do so only if traces of this agent are present. 2,6-Dimethylocta-2,6-diene, however, reacts at 50° C without added hydrogen sulfide, and 2,4-dimethylpent-2-ene does so at 83° C. Whether added initially or not, hydrogen sulfide is always formed during the reaction, and in view of the low product-yields, it apparently exerts an inhibitory effect at higher concentrations, a phenomenon observed in rubber-sulfur vulcanization⁶.

The virtual identity of the products obtained from the Peachey process [procedure (1)] and the present system supports the view that the active sulfuring agent in both cases is S_2 . The precursor of the active S_2 in the Peachey process is possibly a polythionic acid. No evidence about the nature of the precursor in the dithiocarbamate system is available, although Bedford & Sebrell⁸ believe it to be a polysulfide of the type, $R_2N \cdot CS \cdot S_x \cdot Zn \cdot S_x \cdot CS \cdot NR_2$. It is significant that Craig *et al.*⁹ believe that S_2 is the active agent in sulfurations effected by tetramethylthiuram disulfide, and they regard the corresponding thiuram trisulfide as the precursor of S_2 formation.

In order to achieve a more direct comparison with the high-temperature olefin-sulfur reaction, and in the expectation that the differences between the low- and high-temperature Peachey-process products would be simulated, the reaction between 2,4-dimethylpent-2-ene and the dithiocarbamate system at 83° and 140° C was examined. The apparently surprising result was that the products remained at approximately tetrasulfide complexity and retained the dialkenyl unsaturation pattern. However, in judging the significance of this finding, it is necessary to consider observations bearing on the role of zinc compounds in cross-linking reactions.

When 2,4-dimethylpent-2-ene is heated with tetramethylthiuram disulfide alone at 140° C, and alkyl alkenyl polysulfide (average cross-link unit about

S₄) corresponding closely (C/H ratio and infrared spectra) to the product obtained on direct reaction of the olefin with sulfur at 140° C is formed, in addition to the well-known thermal decomposition products of the thiuram disulfide, namely, tetramethylthiourea, carbon disulfide, and sulfur. Sulfuration of the olefin with tetramethylthiuram disulfide at 140° C in the presence of zinc oxide yields a mixture of dialkenyl mono- and disulfides having spectroscopic characteristics closely similar to those of the products obtained from procedures (1) and (2) above. A further contrast with the sulfuration conducted in the absence of zinc oxide was the formation of zinc dimethyldithiocarbamate as the major product of the thiuram disulfide decomposition, although tetramethylthiourea and carbon disulfide were identified as minor products. There was no evidence of olefin-dehydrodimer formation resulting from carbon-carbon cross-linking, as suggested by Farmer¹⁰ and Gee¹¹.

The present results, which extend earlier work of Bloomfield¹² with 2,6-dimethylocta-2,6-diene, find a parallel in Armstrong, Little and Doak's contention¹³ of an exactly similar constitutional change occurring in the products resulting from the interactions of 2-methylbut-2-ene and sulfur at 120–140° C in the absence and presence, respectively, of zinc oxide, mercaptobenzothiazole, and zinc propionate. It is evident, therefore, that zinc compounds profoundly influence the mode of cross-linking, and at high temperatures act to suppress the additive function of alkenylthio groups towards olefin double-bonds by promoting their self-coupling to dialkenyl sulfides. This influence almost certainly accounts for the divergence between the Peachey and the dithiocarbamate-induced sulfuration processes at high temperatures.

EXPERIMENTAL

Microanalyses were carried out under the supervision of W. T. Chambers.

SULFURATION OF OLEFINS BY HYDROGEN SULFIDE AND SULFUR DIOXIDE

Except where stated otherwise, the general procedure adopted was as follows. Sulfur dioxide and hydrogen sulfide were passed alternately into the olefin at 0° C for periods of two hours, this treatment being repeated once or twice. The product was cooled overnight in the refrigerator, volatile material removed under reduced pressure, the residue dissolved in light petroleum (b.p. 40–60°) and kept at 0° overnight to separate dissolved sulfur. The resultant solution, freed from sulfur, was chromatographed on alumina. The eluate contained olefin polysulfides, which were rechromatographed and then cooled to ensure removal of dissolved sulfur. Oxygenated sulfur compounds, adsorbed on the alumina, were removed by elution with ethanol.

(1) *2,4-Dimethylpent-2-ene*, prepared¹⁴ by the pyrolysis over glass wool of 2,4-dimethyl-3-acetoxypentane at 460° C, had b.p. 83°, n_D^{20} 1.4046. Infrared analysis indicated 2% of CH₂:CR₂ unsaturation. The olefin (106 g.), on treatment as described above, gave a crude product (11 g.), separable by fractional elution from alumina into: (1) a pale yellow liquid (0.5 g.) (Found: C, 60.95; H, 9.15; S, 29.7%; atomic ratio C/H, 7:12.6. C₁₄H₂₆S₂ requires S, 24.8; C₁₄H₂₆S₂ requires S, 33.05%); (2) *bisdimethylpentenyl tetrasulfide*, as a pale yellow liquid (6.7 g.), n_D^{20} 1.5670 (Found: C, 52.05; H, 8.1; S, 40.2%; C/H, 7:13.1. C₁₄H₂₆S₄ requires C, 52.1; H, 8.1; S, 39.8%); (3) an orange liquid (0.5 g.) [Found: C, 47.2; H, 7.1; S, 44.4; O (diff.), 1.3. C₁₄H₂₆S₃ requires S,

45.2%]. Elution of the column with ethanol gave (4) a reddish-brown liquid (1.2 g.) [Found: C, 50.7; H, 8.45; S, 31.6; O (diff.), 9.25%; C/H, 7:14. $C_{14}H_{28}O_2S_2$ requires C, 51.8; H, 8.65; S, 29.6; O, 9.9%]. The infrared spectra of fractions (1) and (2) revealed the presence of $R\cdot CH:CR_2$ and some $CH_2:CR_2$ unsaturation. Treatment of the olefin (105 g.) simultaneously with hydrogen sulfide and sulfur dioxide at 83° C yielded: (1) and *olefin trisulfide* (1.8 g.) (Found: C, 57.5; H, 9.5; S, 32.8%; C/H, 7:13.8. $C_{14}H_{28}S_3$ requires C, 57.5; H, 9.6; S, 32.9%; and (2) a *tetrasulfide* (2.7 g.) (Found: C, 51.3; H, 8.3; S, 39.8%; C/H, 7:13.6. $C_{14}H_{28}S_4$ requires C, 51.9; H, 8.65; S, 39.5%). The decreased C/H ratio of these products corresponds to distinct differences in their infrared spectra, compared with those of the low-temperature sulfuration products described above. The high-temperature products show some resemblance to, but not complete identity with, those derived from causing the olefin (50 g.) to react with sulfur (5 g.) for 5 hours at 140°, when a product was obtained that on fractional elution from silica gel gave: (1) (Found: C, 47.9; H, 8.0; S, 44.7%; C/H, 7:14.0); (2) (Found: C, 47.0; H, 7.9; S, 44.85%; C/H, 7:14.1. $C_{14}H_{28}S_3$ requires C, 47.2; H, 7.9; S, 45.0%; C/H, 7:14); and (3) (Found: C, 44.0; H, 7.2; S, 49.1%; C/H 7:13.75. $C_{14}H_{28}S_4$ requires C, 43.3; H, 7.2; S, 49.5%; C/H 7:14).

Treatment of the olefin (50 ml.) with sulfur (5 g.) obtained by passing hydrogen sulfide into benzene saturated with sulfur dioxide, for two days at room temperature, gave a polysulfide (0.3 g.), which was purified by elution from silica gel (Found: C, 50.7; H, 7.8; S, 41.3%; C/H, 7:12.9. $C_{14}H_{28}S_4$ requires C, 52.1; H, 8.1; S, 39.8%).

A mixture of polysulfide (4.5 g.) (Found: C, 51.6; H, 8.05%; C/H, 7:13.1), derived from the hydrogen sulfide-sulfur dioxide sulfuration of the olefin at 0° C, and 2,4-dimethylpent-2-ene (20 ml.) was heated in vacuo for 2 hours at 140°. The product, after removal of the olefin in vacuo, gave a polysulfide (4.8 g.), which was purified by elution from silica gel (Found: C, 52.05; H, 8.2; S, 39.9%; C/H, 7:13.2). The infrared spectrum of this material was indistinguishable from that of the original polysulfide.

(2) 2-Methylpent-2-ene (40 g.) gave a *polysulfide* fraction (2.5 g.) (Found: C, 48.1; H, 7.5; S, 44.6%; C/H, 6:11.2. $C_{12}H_{22}S_4$ requires C, 49.0; H, 7.5; S, 43.6%; C/H, 6:11) whose infrared spectrum showed the presence mainly of $R_2C:CHR$, together with some *trans*- $R\cdot CH:CH\cdot R$ and $CH_2:CR_2$ unsaturation.

(3) 2-Methylbut-2-ene (100 ml.) gave a *polysulfide* fraction (9.5 g.), n_D^{20} 1.6120 (Found: C, 42.2; H, 6.5; S, 51.4%; C/H, 5:9.25. $C_{10}H_{18}S_4$ requires C, 45.1; H, 6.77; S, 48.1%). Infrared analysis indicated the presence mainly of $R_2C:CHR$, together with some $CH_2:CMeR$ unsaturation.

(4) 1-Methylcycloheptene (72 g.) gave a *polysulfide* fraction (2.0 g.), n_D^{20} 1.6280 (Found: C, 51.7; H, 6.85; S, 41.8%; C/H, 7:11.1. $C_{14}H_{22}S_4$ requires C, 52.9; H, 6.9; S, 40.3%), containing $R_2C:CHR$ and possibly a little *cis*- $R\cdot CH:CH\cdot R$ unsaturation.

(5) 2,6-Dimethylocta-2,6-diene (31 g.) gave an orange liquid product, which on fractionation yielded (1) unchanged olefin, b.p. 54–56° (Found: S, 0%), and (2) *didecadienyl tetrasulfide* (8.0 g.) (Found: C, 58.9; H, 8.4; S, 32.7%; C/H, 10:17.1. $C_{20}H_{34}S_4$ requires C, 59.7; H, 8.45; S, 31.8%). Infrared analysis indicated that the major type of unsaturation present was $R_2C:CHR$, but small amounts of $R_2C:CH_2$ and *trans*- $RCH:CHR$ were also present.

A portion (0.6 g.) of the polysulfide typified by fraction (2) (Found: C, 55.3; H, 7.9; S, 36.4%) and 2,6-dimethylocta-2,6-diene (6.2 g.) were heated

under nitrogen for 3 hours at 140° C. Fractionation of the product gave (1) unchanged olefin, b.p. 57–61°/11 mm. (Found: S, 0%); (2) (0.31 g.), b. p. 62–87/11 mm. (Found: S, 1.36%); (3) (0.07 g.), distilling at a bath temperature of 40°/0.005 mm. (Found: S, 11.3%); and (4) a residue (0.52 g.). Elution of a benzene solution of (4) through alumina gave a polysulfide fraction (Found: C, 57.1; H, 8.1; S, 35.2%). The sulfur content of fractions (b) and (c) represents 5.5% of the sulfur present in the original polysulfide.

(6) *Squalene*.—The product from this olefin was washed with water, dried (MgSO_4) and eluted with light petroleum from an alumina column. The eluate, freed from solvent, was subjected to molecular distillation and gave (1) squalene, containing a trace of free sulfur but no cyclic sulfide, and (2) a brown viscous residue, n_D^{20} 1.5310 (Found: C, 74.85; H, 10.3; S, 14.65%; C/H, 30:49.6. $\text{C}_{30}\text{H}_{48}\text{S}_4$ requires C, 76.1; H, 10.35; S, 13.5%).

INTERACTION OF HYDROGEN SULFIDE AND SULFUR DIOXIDE WITH THIOLS

Toluene- ω -thiol, in benzene, was treated alternately with sulfur dioxide and hydrogen sulfide as described above. The product, after chromatographing through alumina, yielded slightly impure dibenzyl tetrasulfide, m.p. 51° (Found: C, 52.1; H, 4.65; S, 43.0. Calc. for $\text{C}_{14}\text{H}_{14}\text{S}_4$: C, 54.15; H, 4.5; S, 41.35%).

Butanethiol, on similar treatment, gave dibutyl tetrasulfide (Found: C, 39.6; H, 7.4; S, 53.2. Calc. for $\text{C}_8\text{H}_{18}\text{S}_4$: C, 39.6; H, 7.45; S, 52.85%).

SULFURATION OF OLEFINS INDUCED BY ZINC DIBUTYLDITHIOCARBAMATE: GENERAL PROCEDURE

A mixture of the olefin, sulfur, zinc dibutyldithiocarbamate, and either zinc oxide or zinc propionate were caused to react under the conditions specified below. In certain cases hydrogen sulfide was introduced into the reaction mixture by passing the gas into the olefin for a few seconds. The product was freed from olefin under reduced pressure, and the extent of reaction was measured by the weight increase of the residue. That portion of the residue soluble in light petroleum (b.p. 40–60°) was cooled to 0° C to remove zinc dibutyldithiocarbamate, and the resultant solution was chromatographed on a column of silica gel (100–200-mesh). The column was developed with (1) light petroleum, giving an eluate comprising olefinic polysulfides containing free sulfur, (2) benzene, which removed zinc dibutyldithiocarbamate, and (3) benzene + 1% of ethanol, which gave a dark red oil containing nitrogen and sulfur. The olefin polysulfide fraction was purified by rechromatographing on alumina or silica gel and cooling the eluate to remove free sulfur.

(1) *2,4-Dimethylpent-2-ene*.—Reaction of the olefin (100 ml.), sulfur (1 g.), zinc oxide (1 g.), zinc dibutyldithiocarbamate (1 g.), and a trace of hydrogen sulfide for 19 days at room temperature gave a polysulfide (0.72 g.) (Found: C, 50.6; H, 7.85; S, 41.6%; C/H, 7:13.0. $\text{C}_{14}\text{H}_{26}\text{S}_4$ requires C, 52.1; H, 8.1; S, 39.8%), and an inhomogeneous fraction eluted by benzene-ethanol (Found: C, 53.3; H, 8.6; N, 2.4; S, 20.25%). Under these conditions 1.3 g. of the olefin had reacted. A similar mixture showed evidence of slight reaction after 4 days at room temperature, but in the absence of hydrogen sulfide no reaction occurred after 7 days at room temperature or 3 days at 50° C. Heating the original reactants for 18 hours at 50° yielded a polysulfide (Found: C, 48.2;

H, 7.45; S, 44.1%; C/H, 7:13.0) whose infrared spectrum was closely similar to those of the polysulfides obtained at room temperature and by the sulfuration with hydrogen sulfide-sulfur dioxide. These reactants, on heating for 4 hours at 83° in the absence of hydrogen sulfide, gave a polysulfide (0.25 g.) (Found: C, 48.8; H, 7.4; S, 42.8%; C/H, 7:12.75), having an infrared spectrum similar to that of the room-temperature product.

Heating a mixture of the olefin (50 g.), sulfur (2 g.), zinc oxide (2 g.) and zinc dibutyldithiocarbamate (2 g.) in a sealed tube for 35 min. at 140° C gave a similar polysulfide (2.7 g.) (Found: C, 49.35; H, 7.7; S, 43.0%; C/H, 7:13.1). Increasing the ratio of sulfur to dithiocarbamate had little effect on the nature of the product: the olefin (50 g.), sulfur (5 g.), zinc oxide (2.5 g.), and zinc dibutyldithiocarbamate (0.25 g.), on heating at 140° C for 30 min., yielded a polysulfide (0.5 g.) (Found: C, 48.9; H, 7.65; S, 43.6%; C/H, 7:13.1) spectroscopically similar to the products described above. An identical product (Found: C, 47.1; H, 7.45; S, 45.35%; C/H, 7:13.3) was obtained after 1 hour at 140° C when the dithiocarbamate in the reaction mixture was replaced by tetramethylthiuram disulfide (0.25 g.).

(2) *2-Methylpent-2-ene* (100 ml.), sulfur (1 g.), zinc oxide (1 g.), zinc dibutyldithiocarbamate (1 g.), and a trace of hydrogen sulfide were caused to react for 2 weeks at room temperature. The polysulfide formed (about 0.2 g.) (Found: C, 44.5; H, 6.75; S, 46.6%; C/H, 6:10.9) was shown by infrared analysis to have largely retained the original $R_2C:CHR$ unsaturation.

(3) *2-Methylbut-2-ene* (200 ml.), sulfur (3 g.), zinc oxide (3 g.), zinc dibutyldithiocarbamate (3 g.), and a trace of hydrogen sulfide, after interacting for 2 weeks at room temperature, gave a slightly impure polysulfide (0.05 g.; olefin reacting, 0.1 g.) (Found: C, 36.25; H, 5.5; S, 51.1%; C/H, 5:9.1), whose infrared spectrum was closely similar to that of the product obtained from the hydrogen sulfide-sulfur dioxide reaction.

(4) *1-Methylcyclohexene*.—The olefin (100 g.), sulfur (2 g.), zinc oxide (1 g.), zinc propionate (0.2 g.), and zinc dibutyldithiocarbamate (2 g.), after interacting for 26 days at room temperature, gave a polysulfide (0.3 g.) (Found: C, 49.4; H, 6.65; S, 42.95%; C/H 7:11.3. Calc. for $C_{14}H_{22}S_4$: S, 40.25%). The same reactants, on heating for 3 days at 50° C gave a polysulfide (0.7 g.; olefin reacting, 1.4 g.) (Found: C, 52.4; H, 6.85; S, 41.05%; C/H, 7:10.9. Calc. for $C_{14}H_{22}S_4$: C, 52.8, H; 6.9; S, 40.25%). A similar experiment under the same conditions gave a polysulfide of higher sulfur content (Found: C, 44.35; H, 5.9; S, 49.3%; C/H, 7:11.2. Calc. for $C_{14}H_{22}S_5$: S, 50.3%). Infrared analysis of the products showed that they were closely similar to each other and to the product obtained from the sulfuration of the olefin with hydrogen sulfide-sulfur dioxide, but were readily distinguishable from the polysulfide (Found: C, 47.8; H, 6.95; S, 45.1%; C/H, 7:12.2. Calc. for $C_{14}H_{24}S_5$: C, 47.8; H, 6.8; S, 45.5%) obtained by heating the olefin (20 ml.) with sulfur (1 g.) for 3 hours at 140° C.

(5) *2,6-Dimethylocta-2,6-diene*.—Treatment of the olefin (50 g.) with sulfur (1 g.), zinc oxide (1 g.), and zinc dibutyldithiocarbamate (1 g.) for 10 days at room temperature resulted in no reaction. Addition of a trace of hydrogen sulfide to the reaction mixture accelerated the sulfuration, giving, after 3 weeks, a polysulfide (0.2 g.) (Found: C, 62.6; H, 9.05; S, 28.5%; C/H, 10:17.35. Calc. for $C_{20}H_{34}S_4$: C, 59.8; H, 8.45; S, 31.9%). The same reactants, on heating at 50° C for 24 hours in the absence of hydrogen sulfide, yielded a polysulfide (0.3 g.) (Found: C, 57.15; H, 8.6; S, 34.4%; C/H, 10:18.1) and appreciable amounts of hydrogen sulfide.

SULFURATION OF 2,4-DIMETHYLPENT-2-ENE WITH
TETRAMETHYLTHIURAM DISULFIDE

(1) The olefin (120 g.) and disulfide (104 g.) were heated in vacuo for 4.5 hours at 140° C. No hydrogen sulfide was detected in the product, which on cooling deposited tetramethylthiourea (44 g.), m.p. 78°. Fractional distillation of the liquid fraction yielded: (1) carbon disulfide (19.6 g.), b.p. 45.5°; (2) unchanged olefin; (3) a fraction, b.p. 79–83°/0.5 mm. (13.6 g.), which, on dissolving in light petroleum (b.p. 40–60°) and cooling, deposited tetramethylthiourea (11.0 g.), m.p. 78°; (4) a fraction, b.p. 90–120°/0.5 mm. (2.6 g.); (5) a fraction, b.p. 120–135°/0.5 mm. (12 g.); and (6) a resinous brown residue, which on trituration with acetone gave sulfur (3.2 g.). Fractional elution of the petroleum-soluble portion of (3) together with fractions (4) and (5) from an alumina column with light petroleum (b.p. 40–60°) gave: (7) a mixture of heptyl heptenyl mono- and disulfides (0.1 g.) (Found: C, 67.1; H, 11.3; S, 21.6%; C/H, 7:14.1. Calc. for $C_{14}H_{28}S_2$: C, 64.8; H, 10.8; S, 24.6%); (8) *heptyl heptenyl disulfide* (2.0 g.), n_D^{20} 1.5084 [Found: C, 65.0; H, 11.1; S, 24.2%; C/H 7:14.3; *M* (ebullioscopic in benzene)], 224; (9) *heptyl heptenyl tetrasulfide* (8.0 g.) (Found: C, 51.8; H, 8.75; S, 39.2%; C/H 7:14.2. $C_{14}H_{28}S_4$ requires C, 51.8; H, 8.7; S, 39.5%); and (10) a residual red oil (2 g.) consisting of higher polysulfides. Intermediate fractions contained an unresolved mixture of sulfurated products (4.9 g.). Infrared analysis of the tetrasulfide (9) showed that this material differs from that obtained by the hydrogen sulfide-olefin dioxide reaction at 0° C but resembles that obtained from the sulfur-olefin reaction at 140° C, though it is somewhat less unsaturated than that from the latter reaction.

(2) A mixture of the olefin (147 g.), the disulfide (120 g.) and zinc oxide (81 g.) was heated in vacuo for 4.5 hours at 140° C. No hydrogen sulfide was detected in the product. The solid portion of the product, on extraction with acetone, yielded zinc dimethyldithiocarbamate (71 g.), m.p. 244°, tetramethylthiourea (1 g.), m.p. 80°, and a yellow liquid sulfide fraction similar to fractions (2) and (3) below. The liquid portion of the product gave on fractionation: (1) unchanged olefin containing a little carbon disulfide; (2) a fraction (7.2 g.), b.p. 83°/0.05 mm.; (3) a fraction (7.3 g.), b.p. 83–123° (mainly 110°)/0.05 mm.; (4) a fraction (4.3 g.), b.p. 123–135°/0.05 mm.; and (5) a residual black tar (6 g.). Fractions (2)–(4) were purified by fractional elution, separately, from alumina by means of light petroleum, giving: (2a) tetramethylthiourea (3.4 g.), m.p. 80°; (2b) a light-yellow sulfide (2.6 g.) (Found: C, 68.55; H, 10.6; S, 20.7%; C/H, 7:13.0); (3a) a yellow liquid sulfide (5.3 g.) (Found: C, 69.45; H, 11.15; S, 19.05%; C/H, 7:13.4); (3b) (2 g.) (Found: C, 57.9; H, 9.0; S, 28.95%; C/H, 7:13.0) having a similar infrared spectrum to that of the tetrasulfide obtained in the low-temperature hydrogen sulfide-sulfur dioxide reaction; and (4a) (3.5 g.) (Found: C, 57.85; H, 9.25; N, 3.35; S, 30.5%; C/H, 7:13.4).

HYDROGENOLYSIS OF POLYSULFIDES WITH LITHIUM
ALUMINUM HYDRIDE¹⁸

The percentage of total sulfur in a polysulfide liberated as H_2S by hydrogenolysis with lithium aluminum hydride, expressed as removable sulfur, was estimated as follows. When the reduction reaction was completed, excess of reagent was destroyed with water, hydrogen sulfide was liberated with dilute hydrochloric acid and transferred by boiling the solution in a stream of nitrogen,

via a reflux condenser, into cadmium acetate solution and estimated iodometrically¹⁶.

(1) *Dibutyl tetrasulfide* (Found: S, 53.2%. Calc. for $C_8H_{18}S_4$: S, 52.9%) (0.2230 g.), when treated under reflux for 4 hours with lithium aluminum hydride (10 ml., 0.5M solution in tetrahydrofuran) in tetrahydrofuran (25 ml.) gave 47.7% of removable sulfur. In a similar experiment, a value of 46.5% of removable sulfur was obtained. The tetrasulfide (0.0658 g.) in ether (20 ml.), when refluxed for 6 hours with an ethereal solution of the reagent (25 ml., 0.25M), gave 52.0% of removable sulfur (theoretical value, 50%).

(2) *Polysulfide from hydrogen sulfide-sulfur dioxide sulfuration of 2,4-dimethylpent-2-ene at 0° C.*—The polysulfide (6.4 g.) in ether was added slowly to an ethereal solution of lithium aluminum hydride (4 g.) and the mixture stirred for 3 hours. Working up the product in the usual way gave *dimethylpentene-thiol* (3.7 g.) (Found: C, 64.3; H, 10.75; S, 24.4%; C/H, 7:14.0. $C_7H_{14}S$ requires C, 64.6; H, 10.7; S, 24.6%), which was unstable and readily polymerized.

(3) *Polysulfide from 2,4-dimethylpent-2-ene-sulfur reaction at 140° C.*—The polysulfide (Found: S, 44.85%. Calc. for $C_{14}H_{26}S_5$: S, 45.0%) (about 0.05 g.) in tetrahydrofuran (20 ml.), when refluxed with lithium aluminum hydride (5 ml., 0.6M in tetrahydrofuran) for the stated times gave the following values for per cent of removable sulfur: 20 min., 45.6%; 30 min., 44.0, 48.0, 54.0%; 60 min., 46.0, 51.0% (the theoretical value is 60%).

Similar treatment of the polysulfide (Found: S, 43.0%) obtained at 140° by sulfuration of the olefin with sulfur, zinc oxide, and zinc dibutyldithiocarbamate gave 51% of removable sulfur.

(4) *Polysulfide from hydrogen sulfide-sulfur dioxide sulfuration of squalene at 0° C.*—This material (Found: S, 13.5%) (0.2541 g.) in ether (20 ml.), on refluxing for 4.5 hours with lithium aluminum hydride (25 ml., 0.5M in tetrahydrofuran), gave 45.5% of removable sulfur.

SUMMARY

The sulfuration of trialkylethylenes with hydrogen sulfide-sulfur dioxide at 0° C (Peachey process) results in disubstitutive cross-linking of the olefins, yielding dialkenyl tetrasulfides. At higher temperatures, substitutive-additive cross-linking occurs, and alkyl alkenyl polysulfides are formed. Dialkenyl tetrasulfides are similarly formed by causing the olefin to react with sulfur at room temperature in the presence of zinc oxide and zinc dibutyldithiocarbamate, low concentrations of hydrogen sulfide acting as a catalyst for this reaction. At higher temperatures, the reaction is also exclusively disubstitutive, a feature connected with the function of zinc compounds in influencing the cross-linking reaction. The sulfuration of olefins with tetramethylthiuram disulfide at 140° C shows a similar influence of zinc compounds.

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STUDIES OF RUBBERLIKE POLYMERS BY NUCLEAR MAGNETISM *

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INTRODUCTION

Rubberlike polymers exhibit characteristic physical properties which set them apart from other solids. An explanation of these characteristic properties is based on the assumption of quasi-free rotation within the long chain molecules which form the rubberlike polymers. The existence and the nature of these internal motions in simpler solids has been investigated by nuclear magnetic resonance absorption and nuclear induction¹. These methods have been extended to the study of polymers². By these methods the degree of rotation and segmental motion, and their changes with varying temperature, cure, loading, and the like can be directly observed in stressed or unstressed polymers.

The spin-spin relaxation time, the magnitude of which is a measure of the freeness of internal rotations in molecules, and the spin-lattice relaxation time were studied for the most part as a function of the temperature and other parameters. Butyl rubber, butadiene-styrene, and butadiene-acrylonitrile copolymers were investigated in greater detail. Other polymers, such as natural rubber, GR-S, polypropylene, polypropylene oxide, and the silicones were investigated more briefly.

At higher temperatures, there is considerable quasi-free rotation leading to narrow line widths. On lowering the temperature, a broadening of the line width results, showing directly the decrease in thermal energies available for rotation.

The effect of cure seems to depend on the particular rubber considered. Natural uncured rubber and one cured with 8 per cent sulfur do not exhibit a marked difference in line width, although the cured sample has a somewhat greater line width for any given temperature. A 50:50 butadiene-styrene copolymer, on the other hand, shows a somewhat higher line width in the cured state.

The effect of carbon loading on the line width seems to be relatively slight, which indicated that loading does not lead to a marked decrease of the degree of rotation, at least in the temperature range from room temperature down to -50°C .

It is possible to draw more quantitative conclusions from line width *vs.* temperature data, and from spin-lattice relaxation time *vs.* temperature curves about the potential barriers hindering rotation. In addition, one can also investigate the line shape as a function of the temperature. Recently Wilson and Pake³ have done this for polyethylene and Teflon. From the analysis of the line shapes obtained at various temperatures, they were able to draw some conclusions about the degree of crystallization in these materials.

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EXPERIMENTAL PROCEDURE

The equipment, and the experimental procedure used in the measurement of the absorption line widths, was for the most part the same as described in our earlier work⁴. The absorption lines were measured in a static field of 6800 gauss. These were detected in the conventional manner by a Twin-T bridge, and recorded from the output of a narrow band lock-in type amplifier on an Esterline Angus milliammeter. Temperatures were maintained to within 1° C, and were measured by a thermocouple imbedded in the sample. Spin-lattice *vs.* temperature data was obtained by the progressive saturation method⁵, which is suitable in the case of broad absorption lines.

RESULTS AND DISCUSSION

LINE WIDTHS FOR NATURAL, SILICONE, AND BUTYL RUBBERS

In our previous work⁴ it was shown that both natural rubber and GR-S have line widths at room temperature of less than 0.08 gauss. This value represented

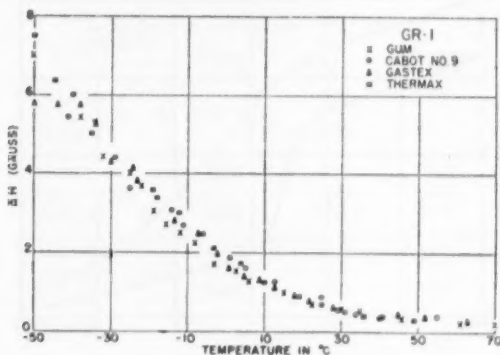


Fig. 1.—Line width *vs.* temperature for Butyl gum (GR-I) loaded with three different carbon blacks.

the lower limit that could be measured with our magnet and was attributed to magnetic field inhomogeneity. In the meantime, the actual line width for natural rubber (smoked sheet) was determined to be 0.06 gauss. Such extremely narrow line widths show directly the high degree of quasi-free rotation of proton groups and of chain segments, proving the basic assumption in the statistical network theory of rubber elasticity.

Narrow lines limited by our field inhomogeneity were found to persist in the case of a silicone oil and two samples of elastomers down to temperatures below -50° C. It is known that silicone rubbers retain their characteristic elasticity and flexibility down to temperatures of the order of -100° C. It seems reasonable to attribute this behavior of the silicones to a greater ease of rotation about Si—O bonds. A further contribution to the line narrowing in the case of the silicones undoubtedly stems from the rotation of the methyl side groups about their C₂ symmetry axis. Powles⁶ has shown, in the case of simple compounds containing methyl groups, that quasi-free rotation takes place at a sufficiently high frequency at temperatures as low as -148° C to contribute to the narrowing of the proton resonance absorption line. Further-

more, in the case of the silicones, the relatively wide separation of the methyl groups, due to the presence of oxygen atoms along the chain skeleton, tends to reduce the steric hindrance to this rotation.

Synthetic rubbers with the exception of GR-S were found to have line widths exceeding 0.1 gauss at room temperature. However, all of the rubbers investigated show a line width behavior at elevated temperatures which is similar to that shown for Butyl in Figure 1. The line width decreases with increasing temperature until it is limited by the resolution of the magnetic field. The line width transition for Butyl is very broad.

EFFECT OF CURE ON LINE WIDTH

Cure increases the line width of both natural rubber and GR-S. Even at room temperatures, the line width is above 0.1 gauss. For natural rubber, the increase is small for samples cured with as much as 8 per cent sulfur. For a 50:50 butadiene-styrene copolymer (Hycar OS-10), the increase in line width

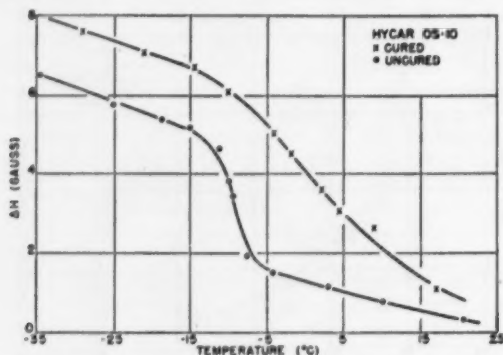


Fig. 2.—Line width vs. temperature for an uncured and a cured butadiene-acrylonitrile copolymer (Hycar OS-10).

with cure is somewhat larger. This is shown in Figure 2. In principle, it should be possible to investigate the mechanism of cure by this method. For instance, a small change in the line width vs. temperature curves could indicate that the curing process involves a physical cross-linking, leading to an increased interaction between adjacent chains. On the other hand, a larger change would indicate chemical cross-linking, which is the process usually assumed. Gutowsky and Meyer⁷ have recently investigated the line width vs. temperature curve for cured natural rubber. This investigation shows that the degree of cure affects to a greater extent the onset of rotation of CH_3 groups than that of segmental motion. From this the conclusion is drawn that cure does not take place by actual chemical cross-linking between chains.

EFFECT OF CARBON LOADING ON LINE WIDTH

The addition of carbon black to a rubber matrix results in an increase of elastic rigidity. This reinforcement by the addition of carbon black has been attributed to strong adsorptive forces between the rubber and the filler. More recently arguments have been presented in favor of a chemical bond between the

rubber and the strongly reinforcing carbon blacks. It is rather difficult to distinguish between physical and chemical forces. In either case, one would expect these forces to immobilize chain segments of the rubber matrix. This additional cross-linkage provided by the carbon-rubber bonds should affect to some extent the rotation and thus the line width. A number of stocks loaded with different blacks as well as different percentages of the same black were studied at room temperature. The results are shown in Table I.

As is evident from these results, no appreciable increase in the width of the absorption line was obtained for the polymers and blacks investigated. The slight decrease observed in line intensity with loading would be compatible with the formation of a few strong bonds between the carbon particles and the rubber matrix, or a large number of physical bonds which are comparatively weak. The latter assumption would seem to be more plausible. In any case the bonds formed produce an effect that is small compared to that produced by vulcanization, and this would further make the assumption of chemical bonding not very plausible.

TABLE I
LINE WIDTH ΔH OF LOADED STOCKS

Parts	Carbon blacks	Hycar OS-10	GR-S	Natural rubber	Butyl
21	Thermax		0.29		
	Wyex		0.27		
	R-40	0.63	0.27	0.32	0.58
	Shawinigan	0.63	0.27	0.25	
40	Philblack	0.63	0.27	0.31	0.63
	Micronex	0.56	0.27	0.27	0.8
	Statex	0.61	0.27	0.29	0.61
	E.P.C.	0.65	0.27	0.31	0.61
	Thermax		0.27		
50	Wyex		0.27		

To compare in greater detail the effect of carbon loading with vulcanization, a study was made of the line width transition for Butyl rubber loaded with 36 parts by weight of Gastex, Thermax, and Cabot No. 9. Butyl rubber was chosen for this study since it is imperative to use systems having the same concentration of cross-links. Butyl is a polymer of limited unsaturation, which reduces considerably the probability of intramolecular linkages. If, in compounding, an excess of sulfur and accelerator is used, a saturated concentration of cross-links results. Therefore, with an excess of curing agents, differences in the adsorptive capacities of the added pigments do not alter the concentration of cross links.

Gastex, Thermax, and Cabot 9 were chosen as pigment fillers, representing roughly particle sizes of 30, 80 and 200 millimicrons, respectively. Gastex and Thermax are channel blacks, whereas the Cabot 9 is a furnace black. This choice of blacks, incorporated in the Butyl matrix, gave three widely different systems. The temperature range studied included -50° to 70° C. There is very little indication of any shift or change in character of the line width transition with change of carbon black filler. A sample of Paracril-35 loaded with 50 parts of Neospectra, a very fine carbon black, exhibited a similar be-

havior. This behavior is in sharp contrast with the effect produced by vulcanization, which broadens the line width transition and shifts the center of the transition to higher temperatures as shown for Hycar OS-10 in Figure 2.

POLYPROPYLENE AND POLYPROPYLENE OXIDE

Line width *vs.* temperature data was taken for the relatively new polymer polypropylene and its oxide, and is shown in Figure 3. The polypropylene had a number average molecular weight of 5000, compared to 4100 for the oxide. The line width for the polypropylene decreased with increasing temperature above room temperature until it was limited by the resolution of the magnet. Below room temperature the line broadens gradually with the line width transition centered at about 10° C. In contrast, the line width for the oxide remains narrow down to a temperature of -40° C, and the line width transition occurs at approximately -50° C. Part of the shift in the line width transition could be attributed to the discrepancy in molecular weights, since the effect of in-

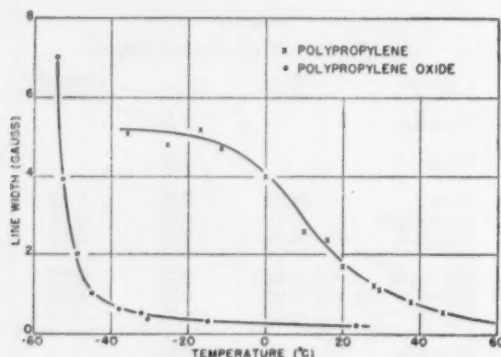


Fig. 3.—Line width *vs.* temperature for polypropylene and polypropylene oxide.

creasing the molecular weight tends to shift in general the line transition to higher temperatures, as was found in studies of fractionated polymers⁴. The drastic change of the behavior of the line width with temperature could be readily explained by the assumption of a greater ease of rotation about C—O bonds in the oxide, compared with that about the C—C bonds in the unoxidized polymer. Also, as in the case of the silicones, the oxygen tends to decrease the steric hindrance to the rotation of side groups.

PARACRIL-35 AND-26

Two samples of butadiene-acrylonitrile copolymers were investigated over a temperature range above the glassy transition region. Paracril-35 contains 65 parts by weight of butadiene and 35 parts of acrylonitrile, whereas the Paracril-26 contains 26 parts of acrylonitrile. The line width transition of the Paracril-35 is centered at about 0° C, compared to that of -7° C for the butadiene-styrene copolymer shown in Figure 4. The Paracril-26 curve shows a transition centered at about -15° C. It is considerably broader than that of the 35 polymer. The greater steepness of the line transition may be due in part to the greater homogeneity realized in the polymer containing the higher

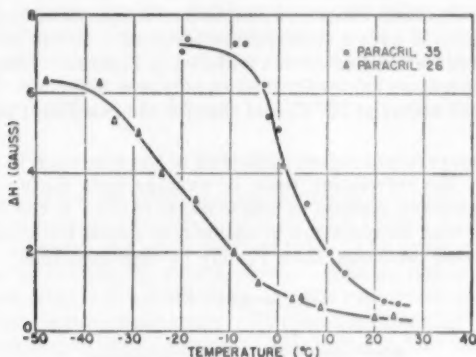


FIG. 4.—Line width vs. temperature for two butadiene-acrylonitrile copolymers (Paracril-35 and-26).

concentration of nitrile groups, since it was found in the case of fractionated polystyrene⁴ that an increased homogeneity produced a similar effect. The increased dipole moment in Paracril-35, compared to that in the 26 polymer would tend to increase the barriers against molecular motion and thus raise the temperature at which the line width transition would occur.

SPIN-LATTICE RELAXATION TIMES

The method of progressive saturation⁶ was used to determine T_1 for samples of raw and cured natural rubber at room temperature. Little, if any, effect on T_1 was observed at room temperature, due to vulcanization. An average value of 0.22 second was obtained for the two samples.

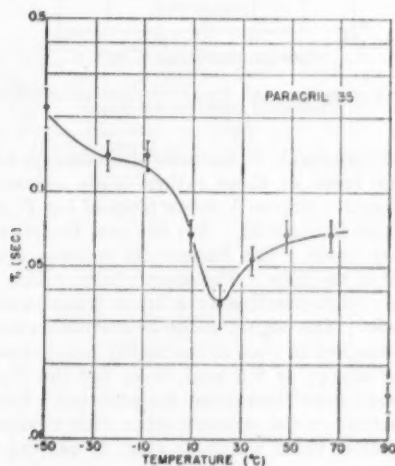


FIG. 5.—Spin-lattice relaxation time as a function of temperature for a butadiene-acrylonitrile copolymer (Paracril-35).

Spin-lattice relaxation times as a function of temperature were obtained for Butyl and Paracril-35 over a temperature range of -50° to 70° C. A T_1 vs. temperature curve for the Paracril-35 is shown in Figure 5. The general shape of the T_1 vs. temperature curves for the two polymers is similar. The minimum for the Paracril-35 occurs at 20° C, and that for the raw Butyl was about 10° C lower.

In the low temperature region to the left of the minimum in the T_1 vs. temperature curves, the correlation time, or average time during which a given molecular configuration persists, is proportional to T_1 . If the variation of the correlation time with temperature is assumed to follow the usual equation for thermally activated processes, then T_1 may be expressed thus:

$$T_1 = Ae^{+V/RT}$$

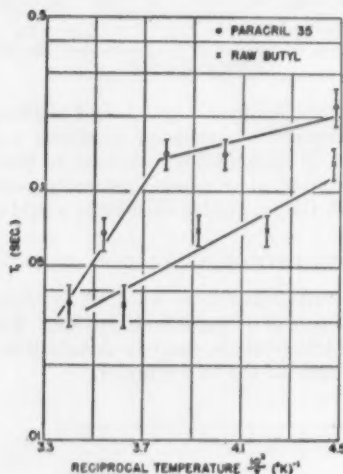


Fig. 6.—Log T_1 plotted against $1/T$ for a butadiene-acrylonitrile copolymer (Paracril-35) and raw Butyl (GR-I).

where A is an arbitrary constant, V , the activation energy, and T , the absolute temperature. On the basis of these rather crude assumptions, activation energies can be computed. Figure 6 shows plots of $\log T_1$ vs. reciprocal temperatures for Butyl and Paracril-35. For the raw Butyl compound, one obtains a value of 2 kcal./mole. The Paracril-35 required two straight lines to obtain a reasonable fit of the data. The steeper slope yields a value of 7 kcal./mole, while the other, corresponding to a lower temperature region, gives a value of 0.6 kcal./mole. The higher value of activation energy obtained for the Paracril is to be expected in view of the highly polar character of this polymer. The activation energy of 0.6 kcal./mole for the Paracril occurs in a region below the second-order transition temperature. One might associate the higher value occurring in the rubbery state with a larger scale segmental motion, whereas the lower value would be more in keeping with the rotation of smaller groups.

Activation energies were also computed from T_2 data, based on an approxi-

mate equation relating the line width and the correlation time introduced by Gutowsky and Pake⁸. Values obtained from T_2 data were considerably higher than those obtained from T_1 measurements. More accurate measurements of the line width are being made at lower temperatures, in the vicinity of the rigid-lattice line width, in an attempt to obtain more reliable values.

SUMMARY

The actual width of the proton resonance line in uncured natural rubber has been determined at room temperature to be 0.06 gauss. Curing of polymers increases the line width at a given temperature. The small increase in natural rubber is possibly compatible with a physical bonding rather than the usually assumed cross-linking. For a butadiene-styrene copolymer, the increase of line width due to cure is somewhat larger. Carbon-black loading increases the line width to a lesser degree than does cure. This is compatible with the concept of physical bonding between the blacks and the polymer chain molecules. Variations of line width caused by changes in chemical composition and copolymerization were also investigated. Polypropylene and polypropylene oxide of roughly the same average molecular weight are compared. The polypropylene oxide exhibits a greater degree of "rotation" about its C—O bonds than polypropylene does about its C—C bonds. Two butadiene-acrylonitrile copolymers also have been studied as a function of temperature. Finally, spin-lattice relaxation time *vs.* temperature studies are reported for a butadiene-acrylonitrile copolymer and for raw Butyl, over the temperature range from -50° to 70° C. Estimates of the magnitude of the barriers hindering "rotation" are made.

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THE RHEOLOGICAL UNIT IN RAW ELASTOMERS*

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INTRODUCTION

In the generally accepted activation theory of viscous flow as developed by Eyring¹ and his many followers, the activated moving units in a flowing liquid are either the molecules of the liquid, or the chain segments of the molecules if the material is a high polymer. However, there are both theoretical and experimental reasons for believing that, at least in many cases, there are coherent masses, containing many molecules of the liquid which move and rotate essentially as rigid units. In organic liquids of low molecular weight, such units are suggested by the x-ray evidence of cybotaxis². Glasses are generally supposed to contain regions of higher and lower order in atomic arrangements³, the regions of higher order being the disperse phase and presumably exhibiting some rigidity and permanence at the lower flow temperature of the glass. Any colloidal material which exhibits thixotropy must pass through intermediate stages of breakdown in which some fragmented thixotropic structures remain suspended in the more liquid phase.

On the basis of the foregoing discussion it would be expected that raw elastomers, which are all highly thixotropic systems, would in their behavior exhibit some evidence of rheological units. Such evidence exists, and is most obvious in the behavior of raw elastomers in milling and calendering operations. When a piece of cold raw rubber is placed on a two-roll mill, the rubber at first tears and shreds as it passes through the nip. As the batch warms up, the sheet becomes smoother and more continuous; but even when fully warmed up, the sheet still shows more or less roughness, depending on the nature of the rubber. A calendered sheet of gum rubber likewise shows more or less irregularity; and the shrinkage after removal from the calender roll is always irregular and develops waves and thickness variations in the sheet. Such irregular recovery indicates the existence of hard and soft regions of macroscopic dimensions in the rubber.

THE THEORY OF CROSS-CURRENT DIFFUSION

There exists a simple method for measuring the mean diameter of the rheological units in an elastomer, if the units are close-packed with a negligible volume of liquid material between them. The method makes use of the fact that all such units will be in rotation in a material subjected to continuous shear.

If a low molecular-weight material, a rubber-soluble dye, for example, exists in high concentration along a plane parallel to the planes of shear, the material will be transferred across the shear planes by rotation of the rheological units just as ink is transferred by a series of inking rollers on a printing press. This cross-current diffusion effect is illustrated in Figure 1. When a dye is being

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transferred by this process, the velocity v of the color front is:

$$v = 2r\omega/\pi \quad (1)$$

When the units are not uniform, the radius r must be interpreted as a mean radius of the rheological units. By the classical theory of the deformation of continuous media, the angular velocity of rotation is expressible in terms of the rate of shear $\dot{\gamma}$ by the equation:

$$\omega = \dot{\gamma}/2. \quad (2)$$

EXPERIMENTAL METHOD

The Mooney viscometer is employed for measurements of the size of the rheological units indicated by the above simple theory. The top surface of a smooth rotor is painted with a rubber cement containing a rubber-soluble dye⁴,

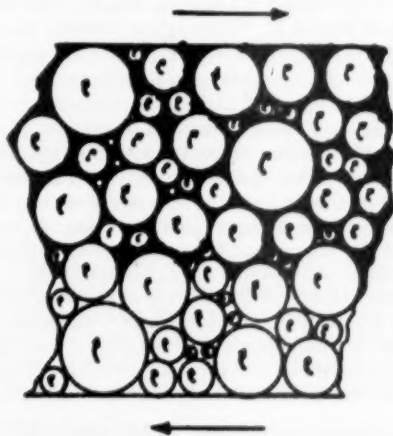


Fig. 1.—Cross-current transfer by rheological units rotating in simple shear. Upward penetration of dye from lower surface is proportional to mean particle diameter, velocity of shear, and total time sheared.

and allowed to dry overnight at room temperature. The dried film is less than 0.001 inch thick, and the concentration of the dye is roughly 300 mg. per gram of dry rubber.

Preformed samples are used to minimize the dye penetration due to flow caused by closure of the viscometer. The sample is preformed in the viscometer at 100° C for several minutes with a spare unpainted rotor. The preformed sample is carefully cut off the preforming rotor and then placed in the viscometer with the painted rotor. After one minute preheating at 100° C the sample is sheared at a fixed rate for a specified time. Sample and rotor are then removed from the viscometer and kept in dry ice until the sample is sectioned for photographing. The photography must be carried out promptly, after warming the sample, to minimize thermal diffusion of the dye.

Radial sections of the sample approximately 1 mm. thick are mounted between two microscope slides, with Arochlor-1262 as the mounting fluid. Photographs by direct light transmission are taken at 5× magnification. The portion of the sample containing dye is opaque and is black on the photographs.

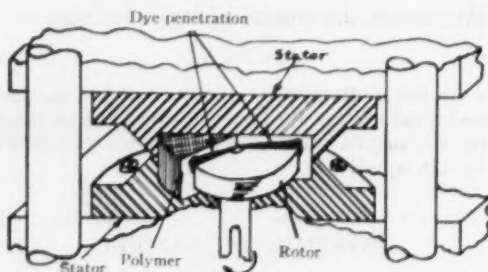


FIG. 2.—Schematic of Mooney viscometer chamber, showing conical color front along radial section.

Theoretically, the color front in a sample sheared with the disk rotor should be conical, as shown in Figure 2. The angle α between the cone generator and the rotor surface, is easily shown from previous equations to be:

$$\alpha = 2rN/h \quad (3)$$

In obtaining this equation, $\dot{\gamma}$ was expressed in terms of time, the radial distance, and N , the total number of rotor revolutions, and h , the distance between the stator and the rotor face. The equation involves the approximation $\tan \alpha \approx \alpha$.

The apex of the cone should lie in the face of the rotor. This ideal condition has never been obtained in experimental work, since the disturbance and flow during closure of the viscometer and the small thermal diffusion during the pre-heat period contribute to the upward displacement of the dye boundary before the sample is sheared. In Figure 3 the effect of shear on diffusion of dye at the center of the sample is shown for several shearing conditions. The penetration at no shear increases in a regular manner with total time in the viscometer at 212° F, but the extrapolation to zero time has a positive intercept that indicates the magnitude of the dye penetration due to closure. The measurements on

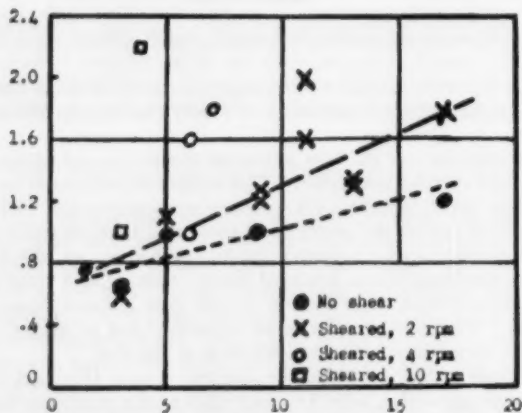


FIG. 3.—Total time in viscometer at 212° F, minutes. Effect of shear diffusion of dye at center of sample.

TABLE I
AVERAGE SIZE OF RHEOLOGICAL UNITS FOUND IN COMMON ELASTOMERS
(All results obtained at a shear rate of 2 rpm)

Polymer	Average diameter of rheological unit (cm.)	Time sheared (min.)	Mooney viscosity (MLA)
Pale crepe	3.1×10^{-4}	20	20
Pale crepe	5.0	15	34
Pale crepe	8.3	12.5	35
Pale crepe	14	8	54
Pale crepe	26	5	76
Butyl, GR-I 15	2.5	10	48
Butyl, GR-I 17	2.5	10	69
Hot GR-S	5.7	16	26
Cold GR-S (X-101)	20	6	29
Paracril-B	13	10	46
Paracril-AJ	23.0	10	44
Paracril-C	36	5	52

samples sheared at 2 rpm show similar results, with extrapolation to zero time giving practically an identical closure penetration. The increased penetration at the center for sheared samples is attributed to transfer of the dye by rheological units rotating in the vicinity of the center line.

The disturbing effects discussed here seem to cause only a constant additive dye penetration, without appreciable effect on the angles of the color front after shear.

EXPERIMENTAL RESULTS

Estimates of the average diameter of the rotating units are obtained by measuring the color front slope on the photographs and calculating the diameter from Equation (3). Although most of the exploratory experiments have been made with Hevea, either pale crepe or smoked sheet, other elastomers have been tested. Table I lists a series of common elastomers and the average size of the rheological unit, found by the simple technique described above.

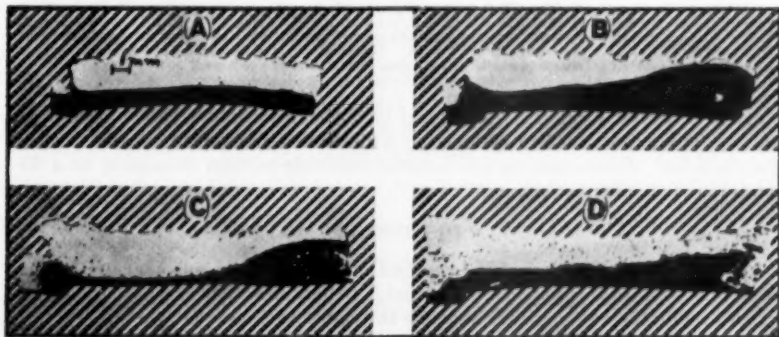


FIG. 4.—Rheological cross-current diffusion in several elastomers. Radial sections are mounted with radius increasing to right. Mooney viscometer rotor speed was 2 rpm. (A) Pale crepe (MLA = 54) in viscometer 8 minutes, but not sheared. Thermal diffusion produces uniform penetration. (B) Pale crepe (MLA = 54) sheared 8 minutes. Note increased dye penetration from lower surface as radius increases towards right. Average diameter is 1.43×10^{-3} cm. (C) Butyl (GR-I 15 MLA = 48) sheared 10 minutes. Low penetration at left center indicates small rheological units. Large penetration at right is from circulation effects at rotor edge. Average diameter is less than 2.5×10^{-4} cm. (D) Paracril-C (MLA = 52) sheared 5 minutes. Occasional irregularities in color front slope indicate presence of larger size particles. Average diameter is 3.5×10^{-3} cm.

Figure 4 contains unretouched photographs of sheared samples and a sample with no shear. All three samples subjected to shear show the typical angled color front, though the angle in 4(C), Butyl (GR-I 15), is very small. The circulation at the edge of the rotor, evident at the right end of Figure 4(C), is the result of secondary stresses developed in the rubber beyond the edge of the rotor. Such circulation effects must be ignored in measuring the color fronts. The basic theory of secondary stresses in a viscoelastic material has been presented by Mooney⁵, among others, in connection with the Weissenberg effect.

In GR-S polymers, White, Ebers, Shriver, and Beck⁶ have shown that the presence of gel alters both the processing and physical properties of GR-S compounds. Gel agglomerates in GR-S have been observed in exploratory cross-current diffusion experiments. In Figure 5 three samples show the turbulent transfer effect attributed to disruption of shear stream lines by large agglomerates of gel. When the sample has no measurable gel, the dye transfer by rhe-

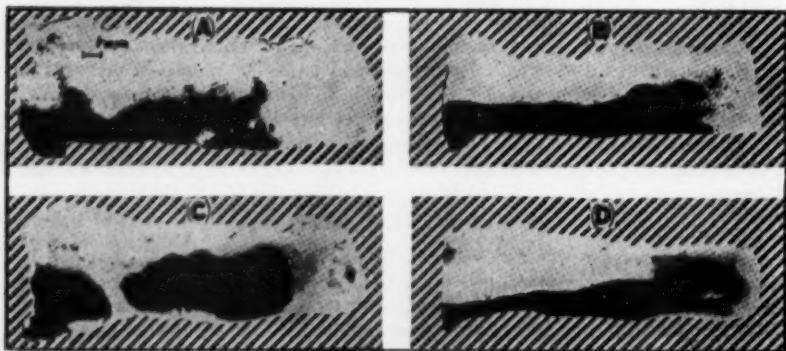


Fig. 5.—Effect of gel in rheological cross-current diffusion. Radial sections are mounted with radius increasing to right. Mooney viscometer rotor speed was 2 rpm. (A) Hot GR-S 122° F (MLA = 45) sheared 5 minutes. Nonuniform color penetration is attributed to large agglomerates that remain intact and rotate under shear. (B) Hot GR-S broken down to MLA = 26. Color front regularity shows agglomerates have been broken up during this type of breakdown. (C) Cold GR-S (X-101) broken down to MLA = 30. Large agglomerates are present after this type of breakdown. Measured gel was 15 per cent. (D) Cold GR-S (X-101) broken down to MLA = 29. Note absence of agglomerates in this special type of breakdown. Measured gel was 0 percent. Rheological unit diameter averages 2×10^{-2} cm.

ological diffusion produces the typical smooth angled color front, as seen in 5(D). The gel content in samples of 5(C) and 5(B) were measured by the standard test of determining the benzene-insoluble portion remaining on a 50-mesh stainless steel screen.

DISCUSSION

It is to be admitted that the method of computing rheological unit diameters presented in this paper is crude and, furthermore, that there is no obvious way to refine the analysis and improve the computations. On the other hand, the computed diameters are presumably correct as to order of magnitude and relative rating.

While the standard Mooney viscometer has been successfully used in the work presented here, the dimensions of this instrument are not the best for this purpose. A similar apparatus built on a larger scale would be better and, in fact, would be necessary for quantitative measurements on samples like that

shown in Figures 5(A), (B), and (C). A design change that would decrease or eliminate the edge circulation would also be a valuable improvement; but none of the minor changes of cavity shape tried in our own work were successful in accomplishing this purpose.

The method described here has been used successfully with rubber mixes containing white fillers. Mixes containing carbon black have not given satisfactory results with any diffusing material tried. Barton and Ganzhorn⁷ have suggested that rheological units may influence carbon black mixing.

The successful experimental demonstration of gross rheological units in elastomers suggests a search for such units in other flowing systems. However, the condition that the diffusing molecules must be small in comparison with the rheological units themselves makes the problem difficult. Perhaps heat conduction is a tool that would work with low molecular-weight liquids. For example, if there are rheological units in water larger than the H₂O molecules, then the thermal conductance between the two cylinders of a Couette viscometer would be increased when the cylinders are kept in relative rotation.

SUMMARY

Reasons are adduced for suspecting that, in a raw elastomer subjected to continuous shear, there exist groups of molecules which are held together by entanglement or by thixotropic attachments and move and rotate essentially as elastic solid bodies. Such coherent molecular groups are called rheological units.

If an elastomer in continuous shear consists essentially of closely-packed rheological units, such units, rolling on each other, will transfer a rubber-soluble dye across the shear planes as the ink rollers transfer ink in a printing press. This predicted phenomenon has been observed with a Mooney viscometer fitted with a smooth rotor, the face of which is covered with a thin film of dried cement containing a dye in high concentration. From the velocity of the color front, a rough value can be computed for the mean diameter of the rheological units. The diameters for a series of different elastomers lie in the range from 1 to 35 microns.

ACKNOWLEDGMENT

The authors are pleased to acknowledge their indebtedness to George F. Schrappe for most of the experimental work in the present paper.

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EFFECT OF MOLECULAR INTERACTION ON THE LIGHT SCATTERING OF RUBBER SOLUTIONS *

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It has been shown in previous publications¹ that such important properties of rubberlike polymers as tensile strength, fatigue resistance, and swelling are, to a great extent, determined by the character and intensity of the molecular interaction of the high polymers.

In this article we shall discuss the influence of molecular interaction in solutions on the nature of molecular light scattering. A study of molecular light scattering makes it possible to obtain very valuable information about the structure of liquids, colloid systems, and molecules, and this method has often been used successfully to solve such problems².

EXPERIMENTAL PART

Solutions of natural rubber (smoked sheet), both unaged and after heat aging in an air thermostat for 18 days at 70° C, were chosen for this study. Solutions of butadiene rubbers containing varying proportions of nitrile groups in the copolymer molecule were studied at the same time.

The natural-rubber solutions were prepared with exclusion of any effects of oxygen. Toluene was chosen as the solvent. All the solvents were dried by calcium chloride, distilled twice over metallic sodium, and filtered twice through a No. 4 glass filter. The rubbers were dissolved after the impurities normally present in smoked-sheet rubber were eliminated. The polymer solutions were filtered several times through a No. 3 glass filter.

The solutions of butadiene-acrylonitrile copolymers were prepared as follows. The polymer was first extracted with distilled water. Methyleneethyl ketone was used as solvent. The product was precipitated by adding methyl alcohol to the solutions. The solutions of butadiene-acrylonitrile copolymers were also prepared by carefully excluding the influence of atmospheric oxygen, i.e., all the operations were performed in an atmosphere of purified nitrogen.

Methyleneethyl ketone was chosen as the solvent because of the good solubility of these copolymers in ketones and the great difference between the refraction indexes of the copolymers and the solvent, which is necessary for accurate measurements of light scattering.

With regard to the solutions of copolymers, it was necessary to keep in mind the fact that in some cases the solutions were not saturated. The solubility of a copolymer, as well as the quantity of precipitant necessary to precipitate the copolymer from solution, depended on the amount of nitrile groups present in the copolymer.

In order to assure accuracy in the measurement of the nitrile group content of the copolymers, the acrylonitrile content of the copolymers was measured both before and after solution (see Table I). The results show that the nitrile

* Translated from RUBBER CHEMISTRY AND TECHNOLOGY from the *Kolloidnyi Zhurnal* (Colloid Journal) Vol. 16, No. 3, pages 171-178 (1954).

TABLE I
ACRYLONITRILE CONTENT IN THE DISSOLVED PHASE OF COPOLYMERS

Polymer	Nitrogen content (%)	Acrylonitrile content (%)
H-6	—	6
H-18	4.6	18.4
H-28	7.4	28.5
H-36	9.5	35.1

Note: The following precipitating agents (methyl alcohol) had to be added to 500 cc. of solvent: H-36 copolymer, 350-400 cc.; H-28 copolymer, 250-270 cc.; H-18 copolymer 150-170 cc.

group content in the dissolved portion of copolymer was practically the same as in the undissolved portion.

The optical apparatus used to measure the intensity of light scattering of polymers is shown schematically in Figure 1. Light from a mercury lamp SVDSH-1000-3 passes through a light filter 2 (with a maximum passage of rays with wave length of about 5460 Å), and then through the condenser 3. The light then enters the chamber of the nephelometer 12. The main part of the pencil of light is directed into the cuvette 5, which contains the solution studied. A small part of the pencil of rays is reflected by a frosted glass plate 4, reduced by a dark element 6, and enters the photometric attachment of a Pulfrich photometer. The light scattered by the solution from the cuvette 5, also enters the photometer, where its intensity is compared with a standard. The other indications in Figure 1 are: 7, a diaphragm; 8, an objective; 9 and 10, prisms; 11, an eyepiece, and 14, a measuring drum.

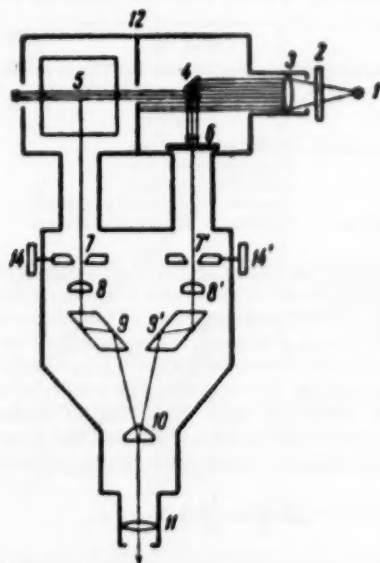


FIG. 1.—Diagram of the optical scheme of the nephelometer (explained in the text)

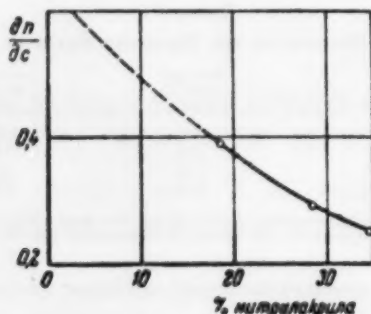


Fig. 2.—The $\frac{dn}{dc}$ value as a function of the acrylonitrile content of copolymers. The abscissa indicates the percentage content of acrylonitrile in the copolymer.

The refractive indexes of solutions of different concentrations were measured by a Pulfrich refractometer. The results of these measurements are shown in Figure 2 and Table II.

The results of measurements of the turbidity of the solvents used were as follows: that of the toluene and 5 per cent methyl alcohol mixture was $2.74 \times 10^{-4} \text{ cm}^{-1}$, that of methylethyl ketone, $1.56 \times 10^{-4} \text{ cm}^{-1}$. The relation of $H(c/\tau)$ to the concentration of solvents is shown in Figures 3 and 4, as well as the calculated values of the molecular weights of the high polymers.

Besides the solutions of substances containing different amounts of atomic groups which are active in the sense of molecular interaction in the chain molecules, it was also interesting to study solutions prepared with solvents of vary-

TABLE II
INDEXES OF REFRACTION OF SOLUTIONS OF VARYING CONCENTRATION

Polymer	Solvent	$H = \frac{32\pi^2 n^2}{3^0 N_A} \left(\frac{\partial n}{\partial c} \right)^2$
H-18	Methylethylketone	17.90×10^{-6}
H-28	Methylethylketone	9.80×10^{-6}
H-36	Methylethylketone	7.19×10^{-6}
Natural rubber	Toluene + 5% methyl alcohol	2.86×10^{-6}
Natural rubber after aging	Toluene + 5% methyl alcohol	2.63×10^{-6}

ing polarity. These solutions can be prepared most easily from binary solvents containing different proportions of polar and low-polar liquids. The turbidity of solutions of natural rubber in toluene and of butadiene-acrylonitrile copolymers in methyl alcohol was measured. The turbidity of the solutions as a function of the methyl alcohol content is shown graphically in Figures 5 and 6.

It was possible to analyze theoretically the results obtained by using the accepted theories of molecular light scattering of high-polymer solutions. Dogadkin, Soboleva, and Arkhangelskaya³ showed the experimental applicability of the following well-known equation for rubber solutions⁴:

$$H \cdot \frac{c}{\tau} = \frac{1}{M} + 2 \cdot B_r \cdot c \quad (1)$$

where H is a constant, measured by refractometry; τ is the turbidity due to the dissolved polymer; M is the molecular weight of the polymer; B_r is a constant

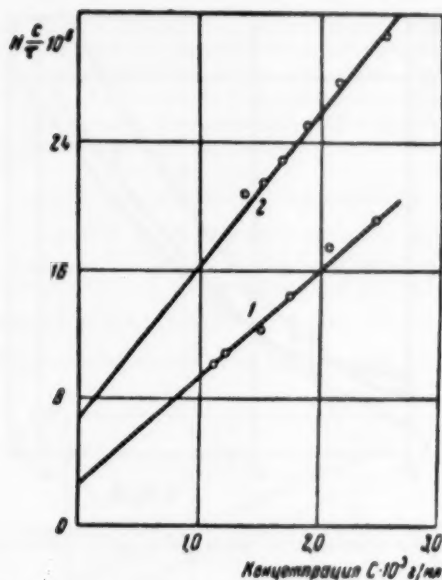


FIG. 3.—The $H(c/r)$ value as a function of the concentration of natural rubber: 1. Before aging; $M = 370,000$; $BT = 6.7 \times 10^{-3}$. 2. After aging; $M = 149,000$; $BT = 9.5 \times 10^{-3}$. The abscissa indicates the concentration $C \cdot 10^3$ per ml.

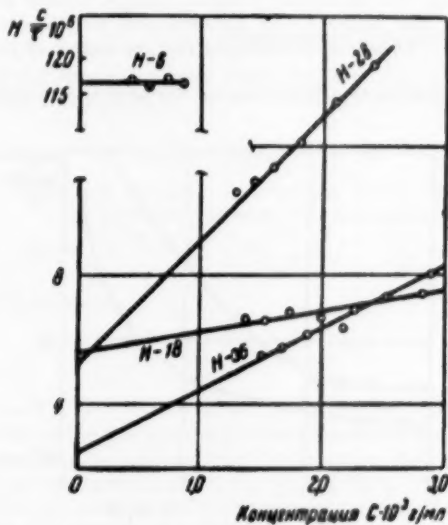


FIG. 4.—The $H(c/r)$ value as a function of the concentration of copolymers: H-28 ($M = 192,000$, $BT = 3.86 \times 10^{-3}$); H-36 ($M = 399,000$, $BT = 1.94 \times 10^{-3}$); H-18 ($M = 180,000$, $BT = 0.67 \times 10^{-3}$) and H-6 ($M = 8600$, $BT = 0$). The abscissa indicates the concentration $C \cdot 10^3$ g. per ml.

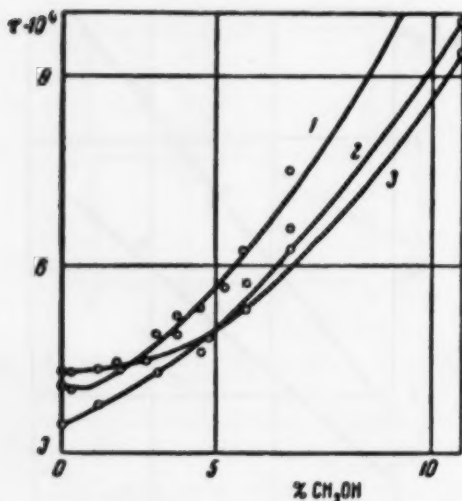


Fig. 5.—Relation of the turbidity of solutions of natural rubber to percentage volume of methyl alcohol. 1. Rubber before aging. 2. After 9 days' aging. 3. After 18 days' aging.

which depends on the solvent and on the polymer, and c is the concentration. Nevertheless, it seemed necessary to confirm the applicability of Equation (1) in the case studied, i.e. the study of light scattering of natural rubber in solution in a binary solvent. The molecular weight of unaged natural rubber measured osmotically, M_{os} , was found to be 370,000, and measured viscometrically, M_{vis} , was 380,000. These values indicate the low degree of polydispersion of this product⁵.

In this case, the close correspondence of the molecular weights as measured

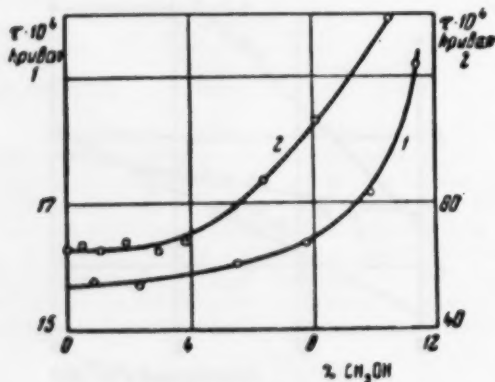


Fig. 6.—Relation of the turbidity of the content of methyl alcohol. 1. Solution of H-28. 2. Solution of H-18. The left-hand ordinate indicates the $\tau \times 10^6$ values of the H-28 polymer (curve 1); the right-hand ordinate the $\tau \times 10^6$ values of the H-18 polymer (curve 2).

osmotically and according to Equation (1), would tend to confirm the applicability of both Equation (1) and the reasoning on which this conclusion is based.

The osmotic measurements of the molecular weight of natural rubber are shown in Figure 7, from which it is seen that, for unaged natural rubber, having a low degree of polydispersion, the molecular weight obtained osmotically is very close to that obtained by light scattering.

INTERPRETATION OF THE RESULTS

Theoretical consideration of the effects of molecular light scattering and osmotic pressure of solutions of high-polymer substances leads to the conclusion that the angular coefficients of the concentration curves: $H(c/\tau) - c$ and $\left(\frac{\pi}{c} - Kc\right) - c$ depend on the intensity and nature of the forces of molecular interaction of the ingredients, as well as on other factors.

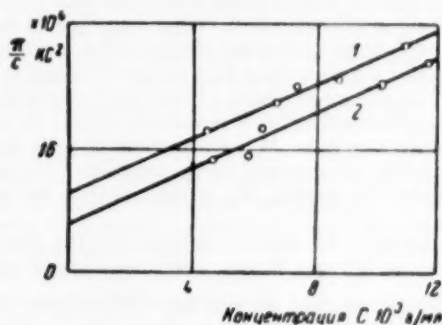


FIG. 7.—Results of determination of molecular weights of natural rubber. 1. After 18 days' aging ($M = 233,000$, $B_\pi = 0.70 \times 10^{-3}$); 2. Before aging ($M = 366,000$, $B_\pi = 0.635 \times 10^{-3}$). The abscissa indicates the concentration $C \cdot 10^3$ g. per ml.

Thus, for example, the angular coefficient of the concentration curve $\left(\frac{\pi}{c} - Kc\right) - c$, which will be designated by B_π , is related to the value of

$$\mu_1 = \frac{\beta}{RT} \cdot V_1 + \frac{1}{z} \left(1 + \frac{4}{3} \frac{v_2}{z} \right) \left(1 - \frac{1}{x} \right) \quad (2)$$

by the following equation:

$$B_\pi = A \left(\frac{1}{2} - \mu_1 \right) \quad (3)$$

where A is a constant. Equation (2) shows that μ_1 depends on v_2 , the molecular fraction of polymers in the mixture, on β , which represents the molecular interaction of the ingredients, on z , the coordination number of the quasicrystalline network, and on x , the degree of polymerization of the polymer.

Using Equations (2) and (3) and the molecular weights of the rubbers, it is easy to show that, in the case of oxidized and unoxidized natural rubber, the change of B_π due to the different values of v_2 and x is so small that it can be disregarded. The variation in the angle of the concentration curves studied is,

consequently, caused principally by the change of the energy factor β , due to the accumulation of polar oxygen-bearing atomic groups in the rubber molecule.

It is interesting to observe that the angular coefficient of the concentration curve, $H(c/\tau) - c$, which will henceforth be called B_τ , is of greater importance than the theory indicates. According to the theory developed by Debye and Einstein, $B_\tau = 2B_\pi$, but this is not always observed in the case of rubber solutions. However, the nature of B_τ and B_π , which determines the increase or decrease of the value of $H \cdot \frac{c}{\tau}$ and $\left(\frac{\pi}{c} - Kc^2\right)$, is the same after an increase of the polymer concentration in the solution.

The increase of π/c with an increase of the concentration indicates an increased tendency of the ingredients to combine as the number of particles of polymer in solution increases. The π/c value of the specific osmotic pressure per unit of concentration represents the tendency of the molecules of solvent to mix with the molecules of polymer. This tendency, which is caused by both entropy and energy factors, may decrease with an increase of the concentration of particles of polymer in solution; on the other hand, the increase may depend on the changes in the entropy and energy factors with the concentration.

However, if the fact is ignored that B_τ is not always equal to $2B_\pi$, the results which are obtained may be inconclusive. Thus for, example, Bechtold⁶ studied the interesting case of simplification of procedures related to the characteristic of polymers with mean numerical M_n and mean relative M_r molecular weights. The characteristic which he proposed for the relation of the mean weight and mean numerical molecular weight, M_z , is derived from the assumption that $B_\tau = 2B_\pi$.

Experimental testing of his method showed that the value M_z represents not only the relation of M_n and M_r but, even more significantly, the absolute values of the molecular weights M_n and M_r . The values: $K_v = \frac{M_r}{M_z}$ and $K_n = \frac{M_n}{M_z}$, which are due to the linear relation with $K_p = \frac{M_r}{M_n}$, are a better characteristic in this sense.

However, the application of M_z in calculations of this kind is only possible when $B_\tau = 2B_\pi$. Since this is not always true in the case of rubber solutions, it is necessary to introduce certain corrections. If, instead of the relation: $B_\tau = 2B_\pi$, which was used earlier, the experimentally obtained relation: $B_\tau/B_\pi = K_1 = 10.56$, is used for unaged natural rubber and $B_\tau/B_\pi = K_2 = 13.59$ for aged rubber, then M_z , which is calculated from the values of M_r and M_n , agrees well with the value calculated from τ and π . The relations of K_v and K_n and K_p , obtained from the experimental data for various natural rubbers, are shown in Figure 8.

In accordance with what has been said, instead of the equation proposed by Bechtold⁶:

$$\frac{1}{M} = \frac{\pi}{R \cdot T \cdot c} - \frac{H \cdot c}{2\tau} + \frac{1}{M}$$

it is necessary to adopt

$$\frac{1}{M} = \frac{\pi}{R \cdot T \cdot c} - \frac{H \cdot c}{K \cdot \tau} + \frac{1}{K \cdot M} \quad (4)$$

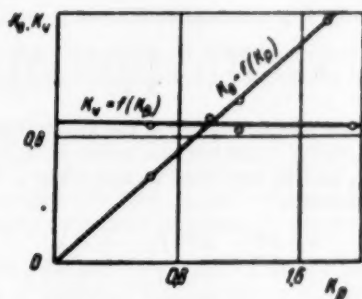


FIG. 8.—Relation of $K_v = M_v/M_n$ and $K_n = M_n/M_v$ to $K_p = M_p/M_n$.

where K is determined experimentally for a given combination of polymer and solvent. Using Equation (4), and knowing one of the values of M_v or M_n , it is possible to determine the other, using only one of the values of the turbidity or osmotic pressure of the solution studied. This is particularly desirable when it is impossible to measure M_v or M_n for the given polymer with sufficient accuracy, e.g., when the dimensions of the molecules are either very large or very small.

Consideration of the data shown in Figure 4 shows the irregular change of the angular coefficients of the concentration curves with an increase of the nitrile groups in butadiene-acrylonitrile copolymers. A calculation showed that the influence of the difference of molecular weights on the inclination of the curves does not exceed 0.6 per cent.

The relation of the angular coefficients of the $H(c/\tau) - c$ curves of the solutions of butadiene-acrylonitrile copolymers to the content of nitrile groups is shown in Figure 9. The irregular change of the angular coefficients of the curves studied is evident from Equation (2). As has already been shown above, the change of B_τ is caused principally by the change in the character of the molecular interaction. According to Equation (3), B_τ changes in proportion to the change of μ_1 , so that it can theoretically assume a value from 0.5 Å (at $\mu_1 = 0$) to comparatively large negative values. In our experimental data, B_τ and, consequently, B_{τ_1} were always positive.

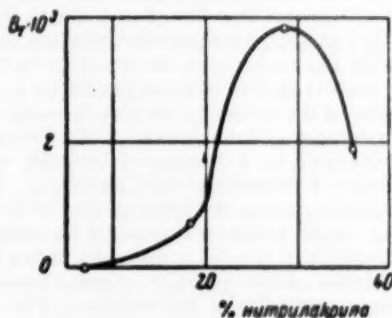


FIG. 9.—Relation of the value of the angular coefficient $H(c/\tau - c)$ to the acrylonitrile content in copolymer solutions. The abscissa indicates the percentage acrylonitrile content.

The value $B_r = 0.5 \text{ \AA}$ is obtained only when $\mu_1 = 0$, that is:

$$\beta = -\frac{RT}{V_1 z} \left(1 + \frac{4}{3} \frac{v_2}{z}\right) \left(1 - \frac{1}{x}\right) \quad (5)$$

this is impossible, since β is the square of the final value and, consequently, is always positive.

The values of B_r and B_r are equal to zero when $\mu = 0.5$. In this case, β must have a definite value:

$$\beta = \frac{0.5 RT}{V_1} - \frac{RT}{V_1 z} \left(1 + \frac{4}{3} \frac{v_2}{z}\right) \left(1 - \frac{1}{x}\right) \quad (6)$$

This value of β is reached when the difference of $\sqrt{\frac{E_1}{V_1}} - \sqrt{\frac{E_2}{V_2}}$ is either negative or positive. A necessary condition here is:

$$\sqrt{\frac{E_2}{V_2}} = \sqrt{\frac{E_1}{V_1}} \pm \sqrt{\frac{1.5 RT}{V_1} - \frac{RT}{V_1 z} \left(1 + \frac{4}{3} \frac{V_2}{z}\right) \left(1 - \frac{1}{x}\right)} \quad (7)$$

In the given case, the accumulation of polar groups must lead to a regular change of the molecular interaction toward an increase of intensity of the orientation and induction interaction. Here the value of E_1/V_1 remains constant, and E_2/V_2 changes. When E_2/V_2 begins to satisfy the condition expressed by Equation (7), $B_r = B_r = 0$. According to Equation (7), this is possible with two values of E_2/V_2 . On the curve shown in Figure 9, the approach of B_r toward zero with a further increase of concentration of polar groups is evident. Analogously, when E_2/V_2 is constant, by changing the solvent correspondingly, it is possible to obtain a curve like that in Figure 9. Knowing the value of E_1/V_1 at which $B_r = 0$, we can determine E_2/V_2 .

Thus, the measurement of $B_r = f(E_1/V_1)$ (where E_1 and V_1 are, respectively, the specific cohesion energy and the molecular volume of the solvent) is a convenient way of determining the specific cohesion energy of the high polymer.

When the effect of the proportion (in percentage) of methyl alcohol on the turbidity of solutions of natural rubber in toluene was measured, an irregular change of the turbidity of the system corresponding to the additions of polar solvent was observed. This phenomenon has already been described by Dogadkin and Soboleva⁷. We assume that the effect is due to the fact that, at first, the addition of methyl alcohol decreases the difference in the nature of the molecular structure of the rubber and its structure in the binary solvent. Further addition of methyl alcohol is accompanied by a new increase of the intensity and character of the molecular reaction between rubber and solvent.

Accordingly, this decrease of heterogeneity of the field of force of the molecular reaction is accompanied by a decrease of intensity of fluctuations and, consequently, a decrease of intensity of light scattering. Further addition of methyl alcohol, by again increasing the heterogeneity of the field of force of the molecular interaction, causes a further increase of turbidity of the solution.

The increase of polarity of the chain molecules of the high polymer is accompanied by an increase of the quantity of polar solvent, the addition of which gives a minimum turbidity of the solution. The resulting change of turbidity due to the increased difference of the refraction coefficients of the polymer and solvent distorts this effect to some degree.

CONCLUSIONS

1. The molecular light scattering of rubber solutions which differ in the polarity of the dissolved high polymer and the polarity of the solvent was investigated.

2. The relation of the angular coefficient of the concentration curves of light scattering to molecular interaction and other factors is discussed theoretically.

3. A relation is proposed which may simplify the procedure of experimentally characterizing polymers by means of the numerical mean and average molecular weights.

4. A method of determining the specific cohesion energy of high polymers according to the data of molecular light scattering in their solutions is offered.

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SOME OSMOTIC MEASUREMENTS OF THE MOLECULAR WEIGHT OF A HIGH MOLECULAR-WEIGHT FRACTION OF RUBBER HYDROCARBON *

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Fractionation of the rubber hydrocarbon in temperate climates has usually resulted in high molecular-weight fractions, with a molecular weight of the order of one million. Bloomfield has shown that fresh latex contains a considerable proportion of hydrocarbon having an intrinsic viscosity (η) of 10 or over and, therefore, a molecular weight of well over 10^6 . The fractionation technique used by Bloomfield in Malaya has now been applied by the writer to smoked sheet and to F rubber, working in the United Kingdom. No very high molecular-weight fractions were found in the smoked sheet, but the F rubber yielded a fraction of (η) = 7.3 and a number average molecular weight 6×10^6 , determined osmotically.

The average molecular weight of natural rubber when freshly prepared is probably well over a million, and includes a substantial portion having a molecular weight of several millions. By the time smoked sheet has reached temperate climates, the high molecular-weight portion has probably been converted to gel. F rubber, presumably because of its different method of preparation, retains the major part of its high molecular-weight material during prolonged storage.

FRACTIONATION

About 4.5 grams of the rubber, cut into thin strips, was allowed to stand in 320 cc. of benzene (all solvents were saturated with nitrogen and solutions were kept in the dark under nitrogen). After two days, the gel was separated by decantation. To the solution, 80 cc. isopropyl alcohol was added, followed by sufficient (265 cc.) of a 70/30 (by volume) isopropyl alcohol-benzene mixture just to produce cloudiness in the solution held at 35° C. The temperature was then allowed to drop to 33.5° C and held constant overnight. The precipitate that settled out was removed and dried on the high vacuum line. The remaining solution was allowed to cool and held at 29.5° C while another fraction separated. A series of fractions were thus obtained by progressively dropping the temperature. The intrinsic viscosity of each fraction was determined in the usual manner by determining the specific viscosity η_{sp} at three concentrations, followed by extrapolation to zero concentration of the straight line relating η_{sp}/C to C .

The results of the fractionation of smoked sheet and F rubber are set out in Table 1.

* Reprinted from the *Archief voor de Rubbercultuur in Nederlandsch-Indië*, Extra No. 2, pages 65-69 (1953).

TABLE 1

Smoked sheet		F rubber	
Percentage	Intrinsic viscosity	Percentage	Intrinsic viscosity
37.4	Gel	25.9	Gel
39.5	5.8	46.5	7.3
0.6	4.1	3.8	4.1
4.0	2.9	3.0	2.9
1.8	2.2	1.4	1.95
6.7	1.6	6.6	1.3
6.0	—	2.6	0.3

Little, if any, degradation occurred during the fractionation: $\frac{\sum(\eta) \cdot \omega}{\sum \omega}$
 = 6.08. The unfractionated F rubber had an intrinsic viscosity of 6.05.

OSMOTIC PRESSURE MEASUREMENTS

Fraction 1 of the F-rubber fractionation was selected for osmotic-pressure determinations. After storage in vacuo, it was sealed in benzene under vacuum. The resulting solution, although very viscous, contained no filterable gel. A master solution of concentration 8.156 g. per kg. was made up by weight. The intrinsic viscosity of the rubber in this solution was determined at the beginning and at the end (3 weeks later) of the osmotic pressure determinations, with the results shown in Table 2 and plotted in Figure 1.

TABLE 2

Prior to osmotic-pressure measurements		After osmotic-pressure measurements	
Concentration (g./100 cc.)	η_{sp}/C	Concentration	η_{sp}/C
0.1174	11.87	0.104	11.27
0.0783	10.31	0.069	9.84
0.0391	8.875	0.034	8.45

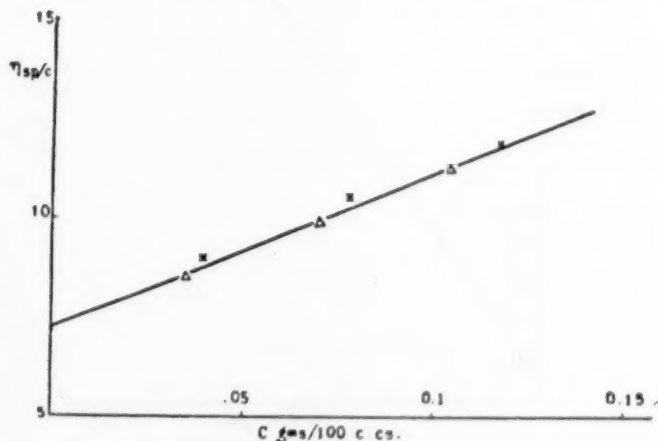


FIG. 1.—Viscosity-concentration relationships of high molecular weight fraction.

TABLE 3

Concentration (g./kg.)	Osmotic pressure π in mm. solution			π/C
	Static	Dynamic	Mean	
2.090	0.71	0.67 0.72	0.70	0.335
2.282	0.94	0.80	0.87	0.380
2.698	1.10 1.15	1.10	1.12	0.415
3.987	2.45	2.38 2.43	2.42	0.607
5.386	4.45	4.47 4.50	4.47	0.830
8.156	—	9.87 10.07	9.97	1.222

The two sets of results fall on the same straight line which extrapolates to $(\eta) = 7.30$, indicating clearly that no degradation had occurred during the period occupied in osmotic-pressure measurements.

Measurements of osmotic pressure were made in a modified Fuoss and Mead stainless steel osmometer, using a reduced collodion membrane. The osmometer was placed in a glass-fronted box contained in a room thermostatically controlled to $25^\circ \pm 0.5^\circ$ C. Thermostatically controlled water was circulated through the osmometer jackets at 25° C. The average zero reading (the difference in levels in the capillaries with both sides of the osmometer filled with benzene) throughout one day was 0.001 cm. and the standard deviation 0.003 cm. The osmotic pressure at six concentrations, prepared by dilution by weight of the master solution was determined both statically and dynamically, with the results set out in Table 3 and plotted in Figure 2.

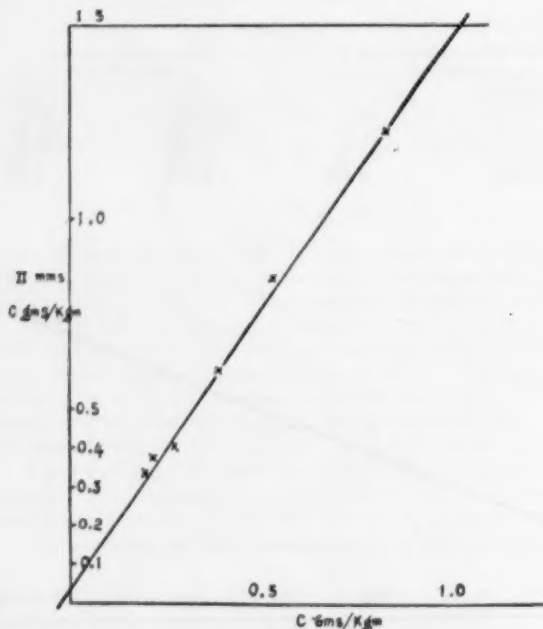


FIG. 2.—Osmotic pressure-concentration relation for high molecular weight fraction of F rubber.

These values fall on a straight line, not on a curve. The intercept at zero concentration is $(\pi/C)_0 = 0.04$, which corresponds to a molecular weight of 6×10^6 . The value, μ , calculated from the slope, is 0.449. This enormous molecular weight is subject to considerable error in the extrapolation of the results, but there is no doubt that the value is of this order.

ACKNOWLEDGMENT

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SMEARING OF VULCANIZED RUBBER *

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INTRODUCTION

Very high localized temperatures may be developed at the rubbing surfaces of materials due to friction, even when there is no noticeable rise of the temperature of the masses. In the case of metals, techniques have been developed to observe and measure surface temperatures generated by sliding¹. For instance, with moderate values of load and velocity, the interface of a lead slider on a steel surface reached the melting point, 327° C. No further temperature rise occurred due to the heat of fusion absorbing the energy.

Such effects should be enhanced in the case of rubber against concrete or asphalt because of the much lower thermal conductivities of these materials and their higher coefficients of friction. A simplified equation applying to equilibrium conditions is sufficient to illustrate the effect of the various pertinent factors in the case¹.

$$T - T_0 = \frac{\mu W g v}{4 a J} \cdot \frac{1}{k_1 + k_2} \quad (1)$$

where:

T_0 — temp. of bulk of material (° C)

T — temp. of interface (° C)

μ — coefficient of friction

W — load (grams)

g — gravity constant

v — velocity (cm./sec.)

a — radius of contact area (cm.)

J — mechanical equivalent of heat (4.2×10^7 ergs/cal.)

k_1 and k_2 — thermal conductivities of the materials $\left(\frac{\text{cal./sec.}}{\text{cm.}^2 \left(\frac{^\circ \text{C.}}{\text{cm.}} \right)} \right)$

For an example involving rubber, the following numerical values were used:

$\mu = 1.0$ (rubber on concrete)

$W = 2110$ grams (for pressure of 30 lb. per sq. in.)

$V = 44.8$ cm./sec. (1 mile per hour)

$k_1 = 0.002 \frac{\text{cal./sec.}}{\text{cm.}^2 \left(\frac{^\circ \text{C.}}{\text{cm.}} \right)}$ (concrete)

$k_2 = 0.0005 \frac{\text{cal./sec.}}{\text{cm.}^2 \left(\frac{^\circ \text{C.}}{\text{cm.}} \right)}$ (tread stock)

$a = 0.56$ cm.

* An original contribution. The paper was presented at the meeting of the Division of Rubber Chemistry of the American Chemical Society in New York, N. Y., September 15-17, 1954.

Substituting these values in Equation (1) gives a value for $T - T_0 = 398^\circ \text{C}$. This value may be questioned, because the velocity assumed may be too high for the equation to apply very exactly, and actually there is a stick-slip action as the surfaces slide, rather than a steady velocity. Nevertheless, it serves to show that high interfacial temperatures undoubtedly occur with loads and velocities of this magnitude.

Although rubber does not have a definite melting point, smearing may occur under such conditions as the above. Practical evidence of this may be seen in the black tracks left on roadways where tires have slid in sudden brake applications.

The abrasion of rubber is a complicated process. The question arises as to the contribution which smearing makes to this abrasion loss under various conditions of road wear and laboratory testing. Smearing of rubber onto the abrasive surfaces of laboratory test-machines has long been recognized as a source of erroneous results and studiously avoided. On the other hand, if it is

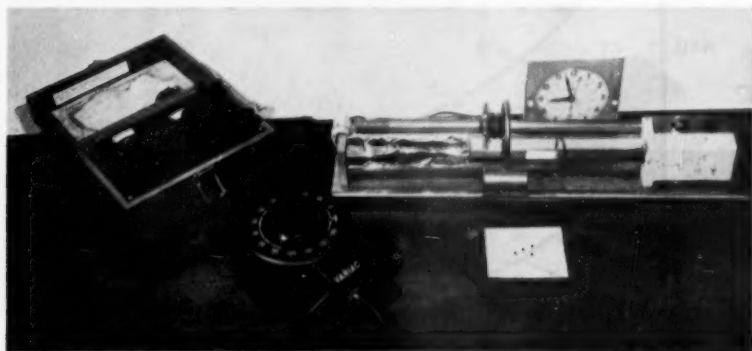


Fig. 1.—Apparatus for smear point determination.

a significant factor and would be expected to contribute to loss on the highway, some way of taking it into account in laboratory evaluation should be evolved.

This work provides a method for measuring the relative smearing temperatures of rubber compounds, and shows how the smear point is affected by compounding variations. In addition, laboratory abrasion experiments in which measured smear temperatures appear to have some significance are described.

EXPERIMENTAL PROCEDURE

Vulcanized rubber does not show a sharp melting point in the ordinary sense. However, a conventional melting point bar (Parr Instrument Co.) may be used with an appropriate technique to measure a smear temperature reproducible to within about $\pm 2^\circ \text{F}$.

In order to prevent corrosion of the bar and attendant difficulties of cleaning, it was wrapped with 0.001 inch thick aluminum foil, held in place with a thin layer of Silicone stopcock grease. The usual thermocouple, which utilized the bar itself as one junction, was replaced by an iron-constantan couple wholly contained in the contact arm. This modified apparatus is pictured in Figure 1.

In use the specimen, a $\frac{1}{4}$ -inch diameter disk, punched out of a tensile test sheet, was placed on the bar with tweezers, the timer was started, and the 20-gram hook weight was placed on it to keep it in intimate contact with the bar. This hook weight was a piece of $\frac{1}{8}$ -inch diameter brass rod bent into a C shape and having an X filed across its contact end so as to provide a knurled surface to prevent sliding off of the specimen. After 30 seconds, the hook weight was used to draw the sample towards the edge of the bar, exerting just enough pressure to prevent the rod from slipping off of the specimen. If a black smear showed on the foil, another sample was put in place closer to the cool end of the bar, and the procedure was repeated. If no smear was produced, the next specimen was moved closer to the hot end of the bar. This trial and error procedure was repeated until a spot on the bar was found where a smear

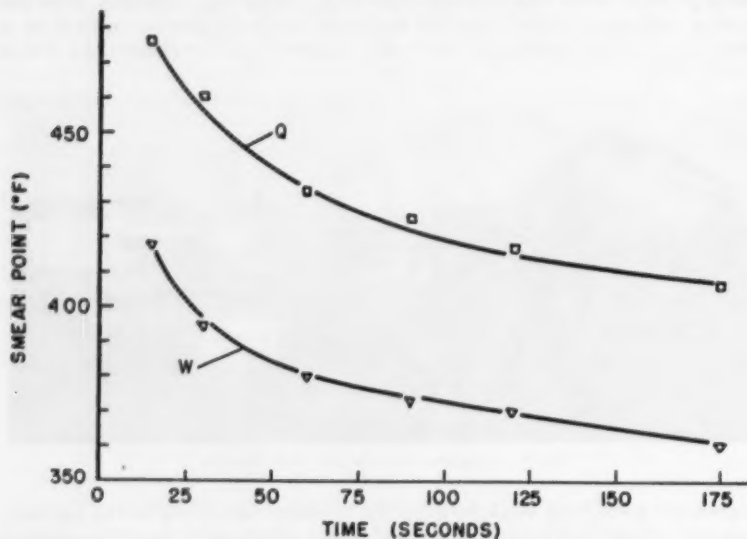


FIG. 2.—Effect of length of time on melting point bar.

was just definitely perceptible. The temperature of this spot was measured with the thermocouple and recorded as the smear point. Although this method has several arbitrary features, it does make possible a relative rating of rubber samples with respect to their smearing tendencies. The relationship between smearing temperature and time on the bar is shown in Figure 2. Selection of 30 seconds as the standard interval was a matter of convenience. Experience was favorable with it for securing reproducible results with a variety of compounds.

COMPOUNDS USED

Formulas for the various compounds used are given in Table 1.

STUDY OF COMPOUNDING VARIABLES

Since the smearing produced seemed to be the result of depolymerization or scission, it was thought that the antioxidant used would have an effect on the

TABLE I
COMPOUND FORMULAS

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z
Smoked sheet	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	70	15	100
Cold GR-S	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	5	3	5	5	5	5	3	3	3	3
Zinc oxide	3	2	2	2	2	2	2	2	2	2	2	2	2	2	2	1	1	1	1	1	1	1	2	3	3	2
Stearic acid	6																							6	6	
Pine tar																				20	3	3	2.75	2.75	2.75	1.75
Red lead	2.75	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5				2							
Sulfur	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1								0.8	0.45	0.45	1.15
Captax																										
Santocure	0.45	2	2	2	2	2	2	2	2	2						1.5	2.0	2.5	2.5	2						
Noba																										
Tuads																				2						
D.P.G.																										
p-Quinone-dioxime																										
Agcrite White	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1											1
Agcrite-HP																										
Phenyl-beta-naphthylamine	1																									
HAF Black	50	35	40	45	50											50	50	50	50	50	50	50	50	50	50	50
EPC Black																										
MPC Black																										

Chemical identification of trade names:

Captax—Mercapto-benzothiazole.

Santocure—N-cyclohexyl-2-benzothiazole sulfenamide.

Noba—N-oxydiethylene-2-benzothiazyl sulfenamide.

Tuads—Tetramethythyuram disulfide.

D.P.G.—Diphenylguanidine.

Agcrite HP—Mixture of phenyl-2-naphthylamine and diphenyl-p-phenylene diamine.

Agcrite White—Symmetrical di-β-naphthyl-p-phenylenediamine.

TABLE 2

Compound	B	C	D	E	F	G	H	I
Parts HAF Black	35	40	45	50				
Parts MPC Black					35	40	45	50
Smear Point ($^{\circ}$ F)	455	452	463	465	461	462	464	475

All cures: 10 minutes at 275 $^{\circ}$ F.

smear point. Several of the more commonly used commercial antioxidants were tried in a technical recipe similar to compound A. These included Agerite-HP, Santoflex-AW, Santoflex-B, Tenemine-2, Thermoflex-A, phenyl-2-naphthylamine, and isopropoxydiphenylamine. No particular antioxidant was outstanding, but increases of 6 or 7 $^{\circ}$ F above the control sample were observed in some cases.

In order to test the effect of initial polymer chain length, compound A was mixed and milled so as to give a range of Mooney values from 70 to 27 ML. These stocks were cured for 75 minutes at 275 $^{\circ}$ F. In no case could a significant difference in smear point be found. The values for all samples fell in the range from 392 to 395 $^{\circ}$ F.

Whether or not carbon black loading affected smear point depended on the vulcanization system. With Captax-Tuads mixtures, an increase of carbon black brought about a rise of the smear point, as shown in the table below.

When a similar experiment was tried with a more conventional compound containing Captax accelerator, the smear point decreased as the amount of carbon black was increased up to 40 parts. Beyond that there was a slight increase. Figure 3 shows these results plotted as a function of modulus at 100 per cent elongation.

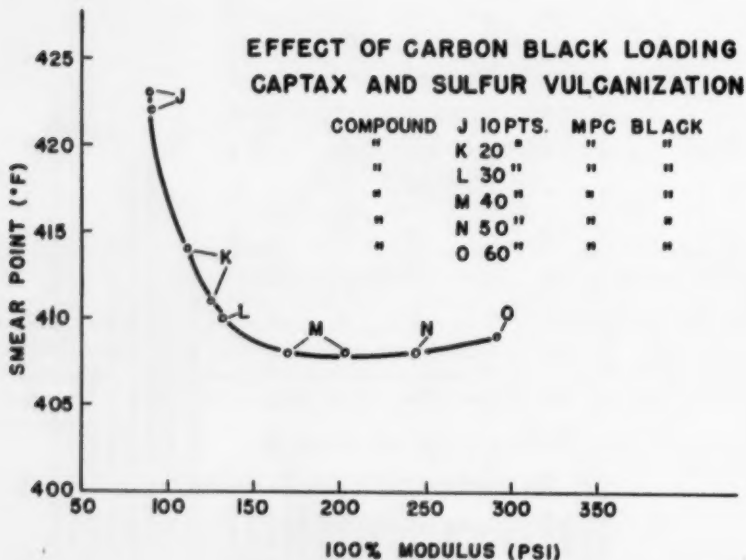


FIG. 3.

The fact that some accelerators such as Tuads gave high smear points, while others such as Captax and Santocure gave much lower values, suggested that the type of cross-linking could have a bearing on the results. There is still a great deal of speculation involved in regard to the chemical nature of the cross-links in vulcanized rubber. But there is definite evidence that vulcanization with Tuads yields carbon-to-carbon or carbon-to-sulfur cross-links² in contrast to the polysulfide cross-links generally assumed to occur with sulfur and most accelerator-sulfur systems. Carbon to carbon cross-links would presumably be much more stable under the smearing conditions than polysulfide cross-links, since the bond energies are usually given as about 58.6 and 27.5 kcal./mole, respectively. The smearing observed is, of course, the result of thermal degradation, a very complex and poorly understood process. The bond energy

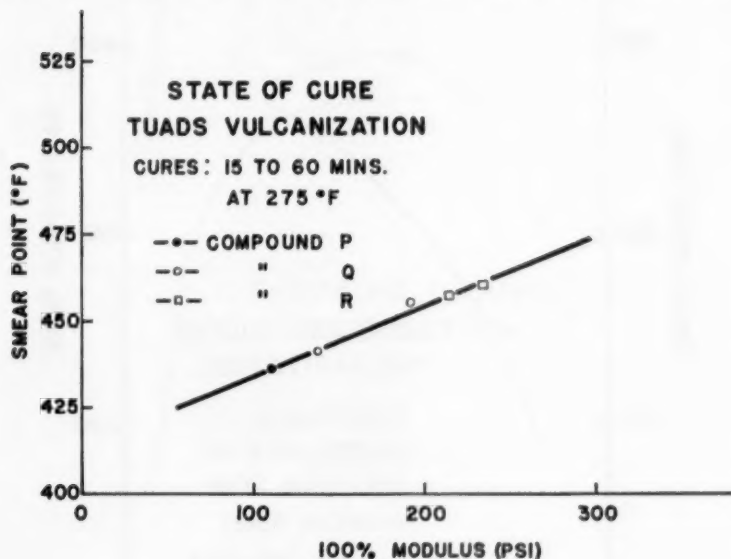


FIG. 4.

of the cross-links may not be the controlling factor in all cases, but its effect did seem to be perceptible in some of the experimental results. This was especially evident in a comparison with the following four vulcanizing agents; Tuads, Tuads plus sulfur, *p*-quinone dioxime, and sulfur.

In Figure 4, the smear point vs. modulus at 100 per cent elongation is plotted for a series of samples vulcanized with Tuads. The modulus at 100 per cent elongation may be regarded as indicative of the amount of cross-linking or density of cross-links. The linear relation between the 100 per cent modulus and the smear point likewise suggests that a close connection exists between the cross-links and smearing.

When a mixture of Tuads and sulfur was used, slightly lower smearing temperatures were observed. It is a reasonable speculation that this may be associated with the formation of some polysulfide cross-links due to the additional

sulfur. As seen in Figure 5, the smear point is not linearly related to the modulus after reversion sets in, but is approximately so up to that point.

Vulcanization with *p*-quinone dioxime gave the highest smear points observed. Here again, the nature of the vulcanizing system is such as to encourage speculation that the high smear point reflects the thermal stability of the cross-link bonds. The nature of these bonds is not definitely known, but they may very well be carbon-to-carbon in this case. As with the Tuads-sulfur

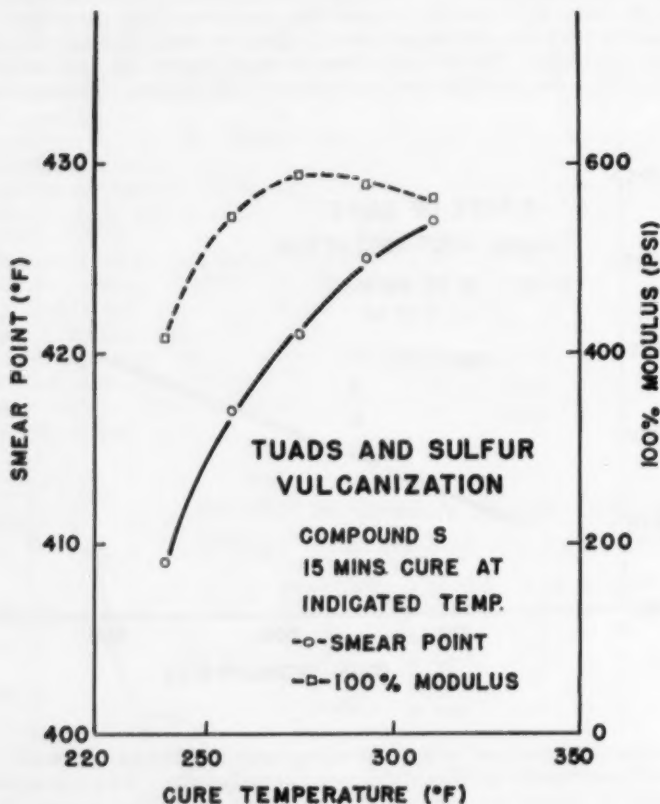


FIG. 5.

cures, the smear point tends to rise slightly after reversion begins. This is shown in Figure 6. Smear points 9° F higher were observed for this compound when cured 90 minutes at 287° F.

The fourth example chosen to try to show a connection between the type of cross-link bond and the smearing was sulfur vulcanization without any accelerator (Compound U). Samples which had been cured for 60 minutes at 293° F were extracted in acetone to remove all free sulfur. They were then dried in a vacuum oven to remove the acetone. Their smear point was 364° F,

which was relatively low compared to those observed when Tuads or *p*-quinone dioxime was used. Although it has not been possible to prove that the number of cross-links and the cross-link bond energy are always controlling for the smear temperature, a close connection is certainly implied by the evidence in the above four cases. A complete explanation of the thermal degradation processes, including the mechanism of the attack on the bonds, would, of course, be required to explain the results adequately.

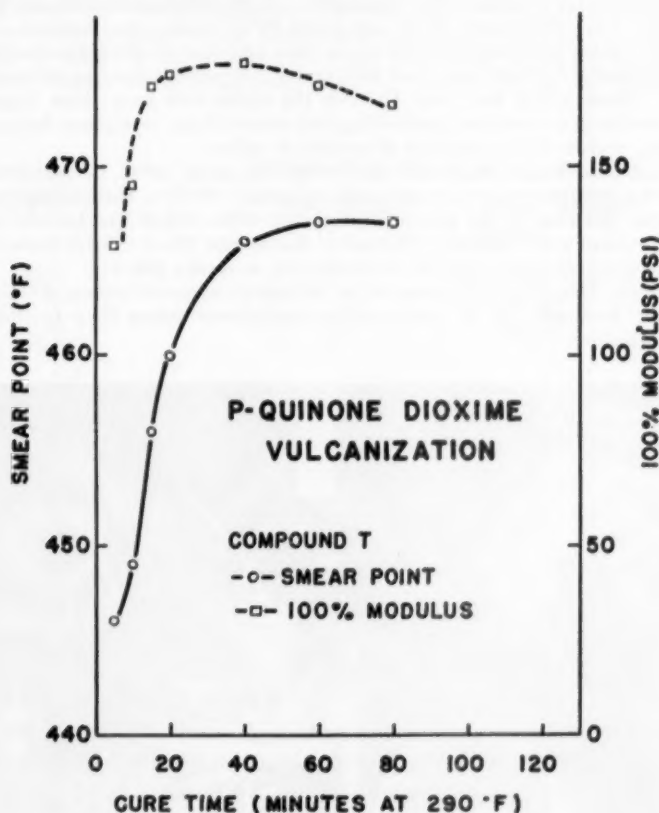


FIG. 6.

In several instances it was observed that excessive bloom on the surface of undercured samples gave an abnormally high smear point. One stock, V, cured with D.P.G., gave a smear point of 442° F before the bloom was removed and 407° F after it was removed by sanding. This suggested that the free sulfur available might be tying the chains back together immediately after they were thermally broken.

To test this theory, a well cured sample of compound W, having Santocure accelerator and sulfur in normal amounts, was soaked in a 5 per cent solution of

TABLE 4

Compound	Z	X	Y
GR-S	100	30	15
Hevea		70	85
Smear point ($^{\circ}$ F)	560+	418	390

All cures: 40 minutes at 310° F.

radioactive sulfur in benzene for 10 minutes. It was then thoroughly dried in a vacuum oven. The smear point was about 40° F higher than normal. The test disks which had been used for smear tests and control disks punched from the test sheet were then extracted with acetone to remove the free radioactive sulfur. Those which had been through the smear test gave three times as many counts as the controls, indicating that cross-linking took place during the smearing process in the presence of unreacted sulfur.

When GR-S tread compounds were tested for smear point, no temperature at which a definite smear occurred could be found. Rather, there seemed to be a gradual charring of the sample. However, when GR-S was blended with Hevea, smears were obtained. Blends of Hevea and GR-S (85:15) showed no increase in smear point; but 70:30 blends did, as shown below.

The smearing frequently observed in laboratory abrasion testing of GR-S is, therefore, probably due to compounding ingredients rather than to thermal degradation.

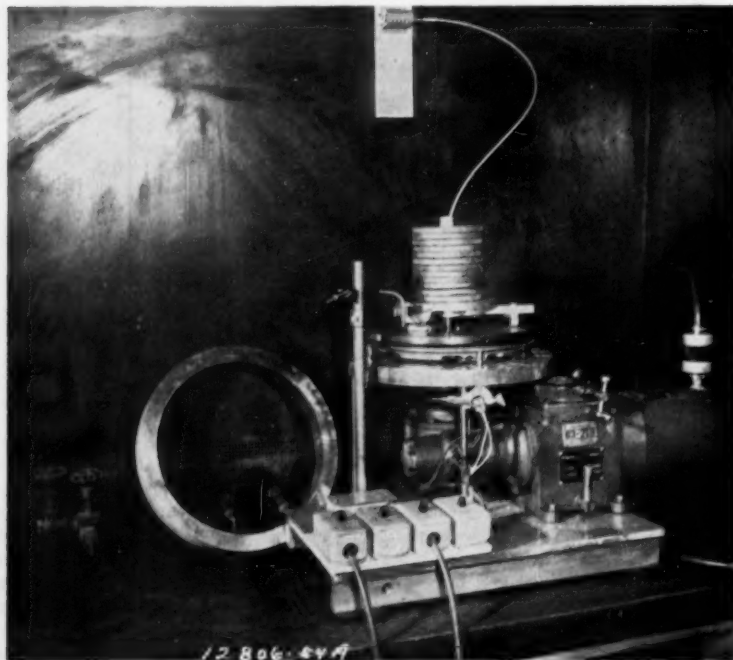


FIG. 7.—Abrasion apparatus.

RELATION OF SMEAR POINT TO ABRASION

The large differences in smear points between natural rubber and GR-S leads to consideration of this factor as at least a partial explanation of differences observed in road performance. Smearing, as was explained at the beginning, would be expected to increase with the load and sliding velocity, that is, with severity of service. Biard and Svetlik³ showed that, in both road and laboratory abrasion tests, GR-S and natural rubber tread stocks were approximately the same under mild conditions; but that when conditions were made more severe, the synthetic tread compounds were much superior. Thus, taking natural rubber to have an index of 100, cold-rubber tread compounds went from a relative rating of 98 under mild conditions to 216 at very severe conditions.

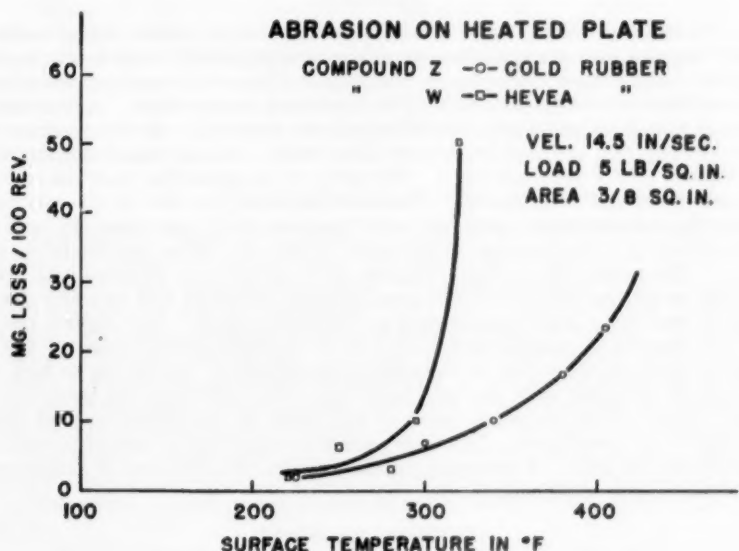


FIG. 8.

Such performance is not explicable on the basis of the ordinary physical properties of the compounds. An explanation may possibly be found in the wide difference in smear points.

To demonstrate, a laboratory machine which would measure smearing tendency as an abrasion loss was devised. A machine previously described⁴ was equipped with a steel plate 12 inches in diameter, having six equally spaced radial grooves of $\frac{1}{4}$ by $\frac{1}{8}$ inch cross-section, as illustrated in Figure 7. The steel plate was heated by two stationary circular radiant heaters installed below and controlled by toggle switches and a Fenwal thermoswitch. The rubber specimens were held stationary and loaded against the plate, which revolved as a horizontal turntable. Loss was measured by weighing the test-specimen.

Figure 8 shows results which were obtained in a comparison of GR-S and natural-rubber tread compounds. The loss for natural rubber begins to rise

rapidly at 300° F, whereas the temperature effect on GR-S is much more gradual, even up to 400° F, the practical limit of the apparatus. The plate was heavily smeared by the natural rubber at 320° F, but there was no indication of smearing of the GR-S, even as high as 400° F.

It is significant that appreciable losses occurred at temperatures lower than our measured smear points. This is probably a reflection of the time-temperature relationship shown in Figure 2.

In relation to road wear, this implies that there can be a gradual thermal degradation of the surface rubber even when conditions are such that the smear temperature is not reached. From all of this it appears that thermal degradation and smearing may be significant factors in road wear, especially under severe service conditions.

SUMMARY

The surface heating which occurs at the interface of rubber sliding under a load may be part of the mechanism of abrasion, especially under severe conditions. Removal of rubber by thermal degradation and a smearing process occurs if the rubber attains sufficiently high localized temperatures. A procedure, using a melting point bar, was developed for measuring the temperature at which smearing occurred for rubber vulcanizates. Smear points reproducible to about $\pm 2^\circ$ F were measured. The effect of compounding variables on the smear point was investigated. The most important variable in this category was the vulcanization system, probably inasmuch as it determined the type of cross-linking. The presence of free sulfur within the rubber also tended to increase the smear temperature. Highest smear points were obtained with mercaptobenzothiazole-tetramethylthiuram disulfide mixtures, and for a non-sulfur compound using *p*-quinone-dioxime as the curing agent. The highest smear point observed for natural rubber was 475° F, obtained with this system. GR-S tread compounds showed no smearing even at 560° F, which was as high as could be obtained with the apparatus used. The resistance to smearing of GR-S may be an important factor in explaining its superiority in road wear under severe conditions. Laboratory abrasion experiments were performed to illustrate the effect of smearing on the relative abrasion loss of GR-S and natural-rubber tread compounds.

ACKNOWLEDGMENT

The authors wish to express their thanks to The Goodyear Tire and Rubber Company and to H. J. Osterhof for permission to publish this work.

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PRESSURE COEFFICIENT OF RESISTANCE OF CONDUCTIVE RUBBER *

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APPARATUS

Hydrostatic pressure was applied to the specimens by immersing them in silicone oil in a stainless-steel pressure chamber. The chamber had an internal capacity of about 20 ml. and was equipped with a $\frac{1}{4}$ -inch steel plunger, with which to apply pressure, and a strain gauge pick-up calibrated up to 16,000 lbs. per sq. in. All the oil seals were made with rubber rings except at the electrical terminals. These were of the conical self-sealing type insulated with Tufnol cones, which also provided the oil seal.

EXPERIMENTAL PROCEDURE

Compounds containing 32, 40 and 70 parts of various carbon blacks were made from natural rubber, Neoprene, polyvinyl chloride, and polyvinyl acetate. The samples were cut from sheet molded on to brass strips, in such a way as to have a width of 7 mm., a thickness of 1 mm., and a brass contact at each end. The distance between contacts was $\frac{1}{2}$ inch or 2 inches, as desired. The Neoprene, polyvinyl chloride and polyvinyl acetate samples had to be given specially bonded contacts. At first, a sample of each length was used for each compound in order to detect possible contact resistance, but after sufficient confidence was gained, only short samples were used as they were more convenient.

In general, a range of pressures from 0 to 6000 lb. per sq. in. was used, as higher pressures could only be obtained by reducing the apparatus volume with packing pieces. Some results were obtained at pressures up to 12,000 lb. per sq. in.

When the pressure coefficient was required at temperatures higher than about 30° C, the samples had to be coated with Thiokol by dipping in a mixture of Thiokol-LP2 and its curing agents. If the samples were not protected, the hot oil altered the sample resistance, and generally the pressure coefficient also during the time necessary for a series of experiments.

STANDARDIZATION OF MEASUREMENTS

The pressure gauge was calibrated up to 5000 lb. per sq. in. against a dead weight tester and found to vary at random in sensitivity by ± 1.5 per cent. The results were plotted using the mean of four such calibrations. The makers' calibration up to 16,000 lb. per sq. in. agreed closely with this mean value.

Resistance readings were measured with resistance ranges of an Avometer type eight, which was compared with a high quality resistance box and found to agree well.

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The temperature of the apparatus was measured to $\pm 1^\circ \text{C}$ by inserting a thermocouple into a pocket in the chamber.

MEASUREMENT OF THE PRESSURE COEFFICIENT OF RESISTANCE

For each sample at each temperature, the resistance R was plotted as a function of the pressure P . Figure 1 is typical. The graphs were all nearly straight in the direction of increasing pressure, and the best straight line was drawn through these points. The pressure coefficient of resistance was defined as the

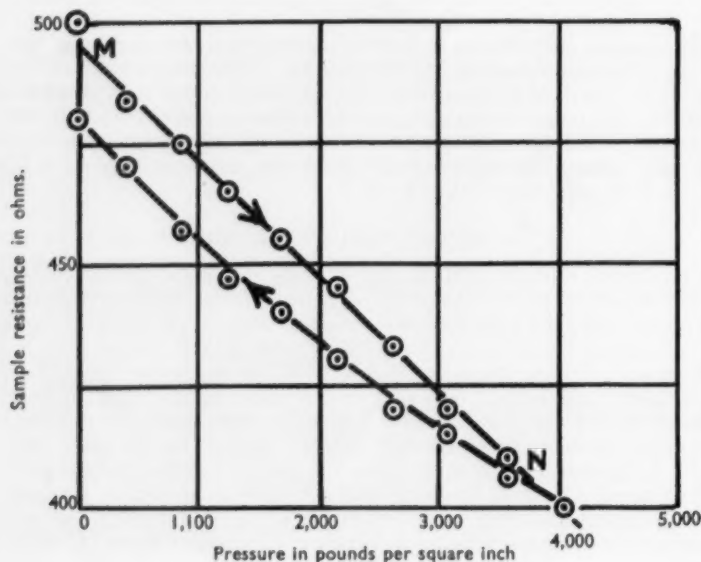


FIG. 1.

quantity, $k = \frac{\Delta R}{\Delta P} \times \frac{1}{R_0}$, where R_0 was the initial resistance of the sample immediately before applying the pressure. $\frac{\Delta R}{\Delta P}$ was the gradient of the best straight line (MN on Graph I).

Some of the compounds tested showed little or no hysteresis, though most did show some. Whether this lack of hysteresis is an invariable property of these particular compounds is not known.

Variation from batch to batch of one compound was tested by taking one sample from each of five independent batches. The standard deviation of the mean of the five was 4 per cent. Variation between samples from one batch was tested by comparing five samples from the batch. Three such sets were taken and yielded standard deviations of the means of 3, 2.5, and 1.5 per cent, respectively.

The pressure coefficient k is thus shown to be a reproducible property of a compound under given mixing conditions.

RESULTS

The values of k (up to a pressure of 5000 lb. per sq. in.) and R_0 , given in the appendix, show that, in a range of sample resistivity of 10^8 ohms, the value of k only varied by a factor of 4 and thus, to a first approximation, k can be regarded as a constant for black-loaded polymers.

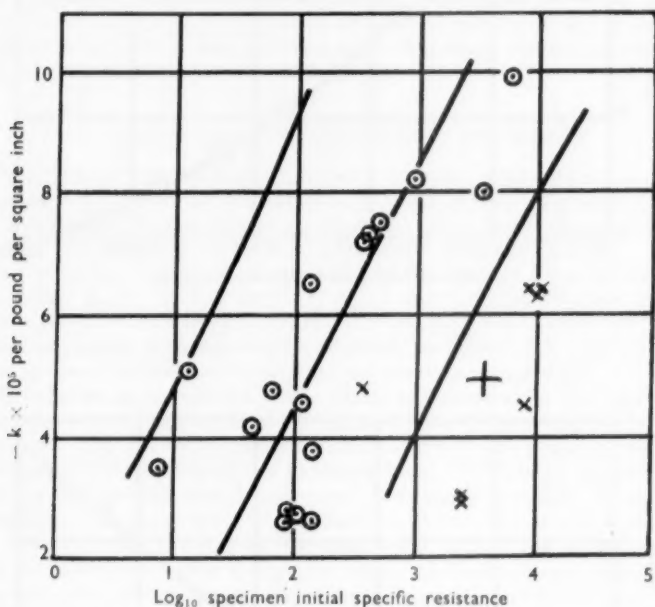


Fig. 2.—Points for low loading rubbers \times . Points for high loading rubbers \circ . Control of low loading points $+$.

Figure 2 shows the general relationship of k to $\log Rt$ and analyses were made to relate the variations of k to such factors as black loading and bulk modulus of the polymer.

All the results for 70 parts and 32 and 40 parts black loading natural rubber are plotted on Figure 2, showing k as a function of $\log 10 R_0$. Statistical analysis shows that, for the high black-loaded compounds, k is related to $\log R_0$. The probability of such an arrangement of points being selected from a random distribution is about 0.01. It is probable, though not beyond doubt, that the low loading results belong to a different population from the high loading results. As can be seen from the graph, the centroid of the low loading points is removed from the high loading line by more than twice the standard deviation for the high loading points.

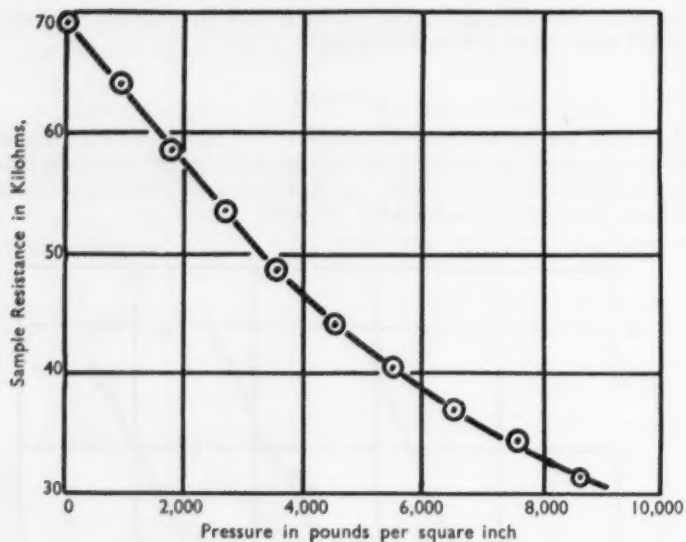


FIG. 3.

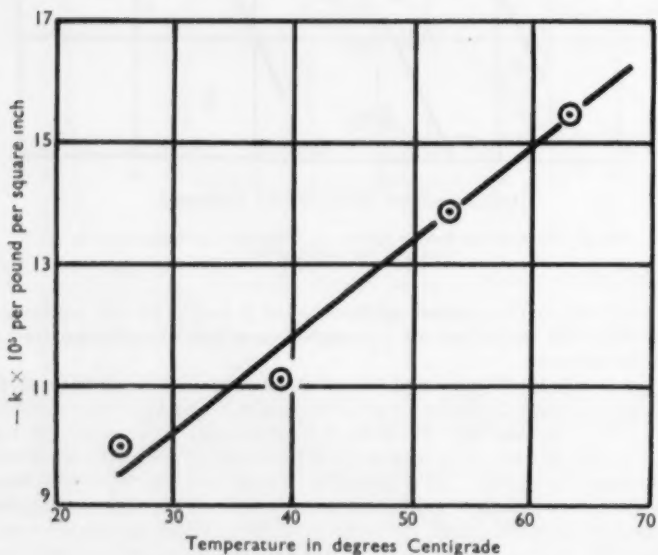


FIG. 4.

No significant effect was found which could be attributed to the bulk modulus.

A few samples were tested to higher pressures than the rest and it was found that, above 5000 lb. per sq. in., there was distinct curvature of the graph of R against P . A typical high pressure graph is plotted on Figure 3.

A sample subjected to the pressure ten times showed a fall in pressure coefficient of 6 per cent. On being left at 5000 lb. per sq. in. for 63 minutes, the sample's resistance drifted down by less than 1 per cent.

All the samples tested at various temperatures showed a rise of the magnitude of k with rise in temperature, of the order of 1.5 per cent per °C. Figure 4 is a typical example of variation of k with temperature. Two polyvinyl acetate samples were found to be very sensitive to silicone oil and, therefore, of doubtful value. They did, however, show that there was no sudden marked change at the second-order transition point.

MECHANISM OF THE EFFECTS DESCRIBED

There are two factors which, at any temperature, affect the conductivity of a sample of a black-loaded substance as hydrostatic pressure is applied. These are the effect of the pressure on the electrical properties of the carbon in each particle, and the effect on the contact between adjacent particles. A black-loaded polymer consists of particles of carbon black of bulk modulus about 5×10^6 lb. per sq. in. in a matrix of polymer of bulk modulus about 5×10^5 lb. per sq. in. On applying hydrostatic pressure, the matrix will contract more than black particles, and so adjacent particles will experience a force pressing them together and increasing the effective contact area.

In order to decide which of these effects was responsible, the following two experiments were made. First, a length of pencil lead was placed in the chamber. This gave random changes of resistance with pressure, which were small compared with the effects in the rubbers. The second experiment was made on a permeable sample composed of 40 parts by weight of Shawinigan non-pelleted black and 100 parts of plaster of Paris. Wires were embedded in this while soft, and the sample was dried at 70° C until the resistance rose no further. The resistance of this plaster sample showed a change of less than 0.1 per cent up to 5000 lb. per sq. in. The zero pressure coefficient in these two samples shows that the bulk effect on the carbon plays only a very small part, since, if the decrease of resistivity in the rubber were due to a change in resistivity in each carbon particle, this decrease must be exactly balanced in these two samples by a process which moves the particles apart as the pressure increased. This would imply a bulk modulus of crystalline calcium sulfate of the order of 5×10^7 lb. per sq. in., which is unlikely.

The significance of surface contamination of the black particles is suggested by the increase of k with R_0 . An alternative explanation is that the high resistance is due to hydrogen absorbed by the carbon black and that the elastic properties of the black are affected by the hydrogen.

A fall of the bulk modulus of the matrix with a rise of temperature would give rise of k . Nolle¹ and various others have measured the velocity of sound in polymers at temperatures between 20° and 50° C. All agree that, in general, it falls by about 10 per cent over this range, corresponding to a fall in bulk modulus of 20 per cent.

CONCLUSION

1. The pressure coefficients of resistance varied only over the comparatively narrow range from -2×10^{-6} to -8×10^{-6} lb. per sq. in. over a range of sample resistance of 10^6 .
2. The temperature coefficient of k was approximately 1.5 per cent per $^{\circ}\text{C}$ for all the samples so tested.
3. The pressure coefficient of resistance was interpreted as a measure of the change in contact resistance between adjacent particles due to the difference in modulus of black and polymer.
4. There was a significant correlation between k and $\log R_0$ for the high loading samples of natural rubber and a probable dependence of k on black loading.

SUMMARY

The pressure coefficients of resistance of several black-loaded compounds of natural and synthetic polymers were measured at temperatures from 0° to 80°C . The effect is shown to be due to variations of the contact resistance between adjacent black particles.

ACKNOWLEDGMENT

The author wishes to thank the directors of the Dunlop Rubber Company Ltd. for permission to publish this paper, and D. Bulgin and D. G. Marshall for their helpful criticism.

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APPENDIX

TABLE I

<i>Formula A</i>	Parts by weight	<i>Formula B</i>	Parts by weight
Natural rubber	100	Natural rubber	100
Sulfur	2.5	Sulfur	3
Santocure	0.5	MBT	1
Stearic acid	2	Zinc oxide	5
Zinc oxide	5	Stearic acid	3
Mineral oil	5	Nonox H.F.N.	1
Nonox H.F.N.	1	Black as otherwise stated	
Black as otherwise stated			

The A or B in the polymer column of Table 2 denotes the formula to which the compound was made.

All samples were cured to obtain optimum mechanical properties.

TABLE 2

Sample No.	Polymer	Black loading	Black	R ₀ short samples only	-k × 10 ³ per p.s.i.	Temp. °C
1	N.R.B.	40	Shawinigan	13 KΩ	4.74	22
2	N.R.B.	40	Shawinigan	—	4.76	22
3	N.R.B.	40	1040	85 KΩ	2.90	22
4	N.R.B.	40	1040	—	3.18	22
5	N.R.B.	70	Shawinigan	237 Ω	3.48	22
6	N.R.B.	70	Shawinigan	—	3.40	22
7	N.R.B.	32	Sph. C	84 KΩ	3.05	22
8	N.R.B.	32	Sph. C	—	3.55	22
9	N.R.B.	70	Sph. C	5 KΩ	3.20	22
10	N.R.B.	70	Sph. C	—	4.36	22
11	N.R.B.	70	1040	2.2 KΩ	4.41	22
12	N.R.B.	70	1040	—	4.92	22
13	N.R.A.	70	Lamp	13.4 KΩ	7.31	22
14	N.R.B.	70	Phil. O	13.0 KΩ	7.22	22
15	N.R.B.	70	Phil. O	126 KΩ	8.06	22
16	N.R.B.	70	Phil. O	35.5 KΩ	8.27	22
17	N.R.B.	70	Phil. O	—	7.70	22
18	N.R.B.	70	Phil. O	—	6.80	22
19	Neoprene	70	Phil. O	23.5 KΩ	6.38	22
20	Neoprene	70	Phil. O	25.0 KΩ	6.77	22
21	Neoprene	70	Phil. O	21.0 KΩ	6.52	22
22	Neoprene	70	Phil. O	—	7.25	22
23	Neoprene	70	Phil. O	—	7.25	22
24	N.R.B.*	70	1040	500 Ω	5.55	22
25	N.R.B.	40	Phil. O	380 KΩ	6.32	22
26	N.R.B.	40	Phil. O	320 KΩ	6.45	22
27	N.R.B.	40	Phil. O	360 KΩ	6.45	22
28	N.R.B.	40	Phil. O	—	5.80	22
29	N.R.B.	40	Phil. O	—	5.98	22
30	Thiokol	50	Phil. O	—	7.25	22
31	Thiokol	50	Phil. O	2 MΩ	7.81	22
32	N.R.A.	70	Stirling L	17.8 KΩ	7.95	22
33	N.R.A.	70	Stirling L	—	7.20	22
34	Neoprene	70	Phil. O	95 MΩ	H. Press	22
35	N.R.B.	70	Phil. O	69 KΩ	H. Press	22
36	N.R.A.	50	Phil. O	17.3 KΩ	5.07	22
37	N.R.A.	50	Phil. O	27.5 KΩ	6.01	22
38	N.R.A.	50	Phil. O	33.5 KΩ	6.19	22
39	N.R.A.	50	Phil. O	1.32 KΩ	6.65	22
40	N.R.A.	50	Phil. O	73.5 KΩ	6.27	22
41	N.R.B.	70	Statex K	4.4 KΩ	6.45	22
42	N.R.B.	70	Statex K	—	6.59	22
43	N.R.B.	70	Phil. E	1500 Ω	4.32	22
44	N.R.B.	70	Phil. E	—	3.97	22
45	N.R.B.	70	Vulc. C	440 Ω	5.01	22
46	N.R.B.	70	Vulc. C	—	5.11	22
47	N.R.B.	70	Statex 125	3.78 KΩ	4.78	22
48	N.R.B.	70	Statex 125	—	4.30	22
49	N.R.B.	70	Sph. N	2.6 KΩ	2.48	22
50	N.R.B.	70	Sph. N	—	2.76	22
51	N.R.B.	50	Sph. C	28.5 KΩ	H. Press	22
52	Pencil	—	Graphite	22.4 Ω	—	22
9	N.R.B.	70	Sph. C	7.7 KΩ	6.20	50
53	N.R.B.	70	Sph. N	3.4 KΩ	2.71	23
53	N.R.B.	70	Sph. N	3.42 KΩ	2.91	37
53	N.R.B.	70	Sph. N	3.40 KΩ	3.52	45
53	N.R.B.	70	Sph. N	3.42 KΩ	3.88	55
53	N.R.B.	70	Sph. N	3.50 KΩ	4.27	71
53	N.R.B.	70	Sph. N	3.50 KΩ	4.50	81
53	N.R.B.	70	Sph. N	3.48 KΩ	2.70	23

TABLE 2—(Continued)

Sample No.	Polymer	Black loading	Black	R ₀ short sample only	-k × 10 ⁴ per p.s.i.	Temp. ° C
54	N.R.B.	70	Sph. N	4.8 KΩ	2.61	23
54	N.R.B.	70	Sph. N	4.90 KΩ	2.96	37
54	N.R.B.	70	Sph. N	4.93 KΩ	3.50	45
54	N.R.B.	70	Sph. N	5.0 KΩ	3.90	55
54	N.R.B.	70	Sph. N	5.3 KΩ	4.69	71
54	N.R.B.	70	Sph. N	5.4 KΩ	5.16	81
54	N.R.B.	70	Sph. N	5.3 KΩ	1.34†	23
55	N.R.B.	70	Sph. N	3.03 KΩ	2.79	24
55	N.R.B.	70	Sph. N	3.02 KΩ	3.09	39
55	N.R.B.	70	Sph. N	2.90 KΩ	3.66	60
55	N.R.B.	70	Sph. N	2.76 KΩ	3.06	46
55	N.R.B.	70	Sph. N	2.78 KΩ	2.05	18.5
56	Neoprene	70	Phil. O	60 KΩ	9.05	24
56	Neoprene	70	Phil. O	76 KΩ	10.38	39
56	Neoprene	70	Phil. O	69 KΩ	12.48	60
56	Neoprene	70	Phil. O	67.5 KΩ	10.93	46
56	Neoprene	70	Phil. O	36 KΩ	6.98	18.5
57	N.R.B.	32	Sph. C	295 KΩ	4.53	25.4
57	N.R.B.	32	Sph. C	293 KΩ	4.97	39.0
57	N.R.B.	32	Sph. C	295 KΩ	6.38	53
57	N.R.B.	32	Sph. C	287 KΩ	6.90	63
58	N.R.B.	70	Phil. O	212 KΩ	9.95	25.4
58	N.R.B.	70	Phil. O	239 KΩ	11.12	39
58	N.R.B.	70	Phil. O	323 KΩ	13.9	53
58	N.R.B.	70	Phil. O	400 KΩ	15.5	63
59	P.V.C.	75	1040	3.5 MΩ	5.65	24
59	P.V.C.	75	1040	3.4 MΩ	5.45	35
59	P.V.C.	75	1040	4.0 MΩ	7.57	45.5
59	P.V.C.	75	1040	4.0 MΩ	7.12	60
60	Near-Ebonite	43	1040	305 Ω	3.68	24
60	Ebonite	43	1040	330 Ω	3.38	35
60	Ebonite	43	1040	410 Ω	5.05	45.5
60	Ebonite	43	1040	460 Ω	5.26	60
61	P.V.A.	70	—	17.0 KΩ	5.03	1.7
61	P.V.A.	70	—	20.0 KΩ	7.35	10
61	P.V.A.	70	—	23.0 KΩ	5.61	20
61	P.V.A.	70	—	23.0 KΩ	4.71	29†
61	P.V.A.	70	—	13.2 KΩ	4.60	40†

* Swelled with 2.5 per cent by weight of paraffin.

† Attacked by the silicone oil.

FORMATION OF RUBBER FILMS FROM SOLUTIONS AND AQUEOUS DISPERSIONS *

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One of the reasons for the direct application of latex in the manufacture of rubber products is the high tensile strength of the latter compared with the tensile strength of products prepared from rubber solutions. Although this has been known for a long time, there has been no explanation of the fact in the scientific literature, with the exception of certain references to the influence of milling of rubber before preparing its solutions. A decrease of tensile strength actually does result from the milling of natural rubber, due to oxidative destruction which occurs during this process¹. However, Voyutskii and Dzyavel² showed that latex films are stronger than corresponding films prepared from rubber solutions, even when the solutions are prepared without previous milling of the rubber.

The reason for this greater tensile strength of latex films must be sought in the unique structure of the films, which is different from the structure of films prepared from solutions. A latex film can be represented schematically as composed of rubber particles, enveloped by a protective layer of nonrubber substances (albumins, resins, soaps, sulfur compounds, etc.). These protective envelopes of the individual particles touch each other, forming a network throughout the mass of the integral film of rubber. However, at various points in the network there are ruptures and, at these points, there is evidently contact and coalescence of the rubber component of the particles. In a film from a rubber solution, the substances of the protective layers do not form a continuous solid phase, but are dispersed in the rubber hydrocarbon. The existence of a network of nonrubber substances in the latex film is reflected, not only in the value of the tensile strength, but also in a number of other properties of such films.

The number of publications dealing with the structure of latex-rubber films is small³; some are studies concerned with the structure of films of vulcanized latex⁴, others of films containing various fillers⁵. Here a more complicated system is involved, and the role of the nonrubber network can not be studied independent of other factors.

The purpose of the present study is to explain the influence of the structure of latex rubber films on some of the properties of such films.

EXPERIMENTAL PART

Films prepared from natural latex (Revertex and Jatex) and from synthetic butadiene-styrene latex (Igetex-S) were studied, as well as films from solutions of the corresponding dry rubbers. The latex films were obtained either by repeatedly dipping glass plates 9×12 cm., in latex, or by pouring latex onto glass plates or tightly stretched cellophane. The concentrations of all the latexes

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Kolloidnyi Zhurnal* (Colloid Journal), Vol. 15, No. 6, pages 448-454 (1953).

were brought to the same value, viz., 38 per cent. The films were dried in most cases at 70° C for 10–12 hours, and then brought to constant weight in a vacuum. Special experiments showed that films dried for two days at 26° C and for 12 hours at 70° C had the same mechanical properties. These latex films were next dissolved in benzene. The solution (2.5 per cent) was poured onto stretched cellophane and evaporated at 70° C for 12 hours; the films were then brought to constant weight in a vacuum. The thickness of the latex films was the same as that of the films from solutions, viz., 0.17–0.20 mm.

TABLE I
MECHANICAL PROPERTIES OF FILMS PREPARED FROM LATEX
AND FROM SOLUTION

Material	Tensile strength (kg. per sq. cm.)	Relative elongation (%)	Modulus at 100% (kg. per sq. cm.)	Residual elongation (%)	Residual stress (%)
Revertex	8.2	775	1.3	33	45
Natural-rubber solution	4.5	575	4.2	10.3	72
Igetex-S	3.8	625	3.5	30.	15
Buna-S solution	2.0	375	1.7	7.8	50

The mechanical properties of the films were measured on a precision dynamometer, with the lower clamp moving at a rate⁶ of 10 mm. per min. The specimens were cut out in strips 10 mm. wide and 30 mm. long, and the length of the section measured was 10 mm. Tensile strength, relative elongation at rupture, dynamic modulus, residual elongation after stretching to 300 per cent, and stress relaxation after stretching to 200 per cent were all measured.

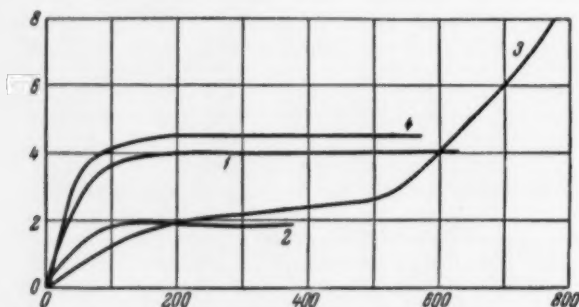


Fig. 1.—Stress-strain curves of films: 1. Latex. 2. Buna-S solution. 3. Revertex. 4. Natural rubber. The abscissa indicates the elongation at rupture in percentage; the ordinate the tensile strength in kg. per sq. cm.

The residual elongation was measured after one day's rest and immersion for 30 minutes in water at 70° C. It is seen from the results obtained, which are presented in Table I and Figure 1, that latex films differ from films from solutions of the corresponding rubbers, not only in their tensile strength values, but also in the shape of their stress-strain curves and in a number of other mechanical properties.

In films from solutions, the relative elongation and residual elongation are lower, but the residual stress is greater than that of films from latex. This is a general phenomenon, and it does not depend on the type of polymer.

It is interesting to confirm the presence of stresses which are set up during the formation of the sheets, as a result of the holding action of the supporting surface and which remain in the final film. As Kargin and Shteding have shown⁷, the shrinkage of films which takes place during the disappearance of stresses under conditions favorable to rapid relaxation is a measure of these internal stresses.

To study this, disks of 25 mm. diameter were cut out of the films prepared from solutions and from latexes on a solid surface (glass plate or cellophane) and, in turn, on a liquid (water or mercury). Two lines at right angles to each other were drawn on them with a pencil, near the end of the specimen. The glass films were then suspended in benzene fumes, allowed to swell for three days, and then dried to constant weight in a vacuum. The length of the lines drawn was measured by a microscope with an accuracy of 0.001 mm., the thickness of the films was measured with a micrometer with an accuracy of 0.01 mm.

TABLE 2
SHRINKAGE OF FILMS PREPARED FROM LATEX AND FROM RUBBER SOLUTIONS

Material	Base	Percentage change of initial values		
		1st Diameter	2nd Diameter	Thickness
Revertex	glass	0	0	0
	cellophane	0	0	0
	mercury	0	0	0
Jatex	cellophane	0	0	0
Igetex-S	glass	-3	-3	7
	cellophane	-3	-3	7
	mercury	0	0	0
Natural-rubber solution	glass	-8	-10	20
	cellophane	-7	-10	17
	water	0	0	0
Buna-S solution	glass	-14	-15	36
	cellophane	-14	-14	40
	mercury	-7	-7	16

The percentage contraction was calculated from the decrease of length of the lines and the increase of thickness of the film. The results obtained are presented in Figure 2.

These data show a sharp difference in the extent of the contraction of films prepared from latex mixtures and from solutions. In the first case there is no contraction, or it is very slight (in the case of Igetex); in the second case it reaches a very large value, particularly in the case of a film from Buna-S solution. Films prepared from this solution shrink on mercury although liquid supports, e.g., mercury or water, it would seem, can not exert a holding action during formation of a sheet, but would be expected to allow free contraction under the influence of the internal stresses which appear in it.

Since the substances which form the surface layer of rubber particles in latex are hydrophilic, in contrast to a hydrophobic polymer, one might expect that films from latexes and from solutions would swell in water in different ways. In order to exclude the effect from water-soluble substances being leached out, the specimens were swollen in water vapor.

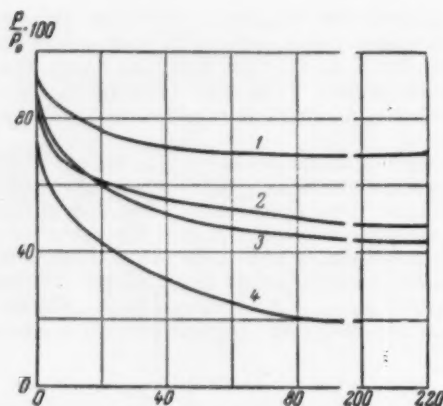


FIG. 2.—Stress relaxation of films: 1. Natural-rubber solution. 2. Buna-S solution. 3. Revertex. 4. Igetex. The abscissa indicates the time in minutes.

The degree of swelling was determined as the ratio of the greatest increase of weight of a film to its initial weight. One might expect that latex films, in which the hydrophilic substances form a dispersion medium, would swell more than films prepared from solutions. The results shown in Table 3 show, however, the opposite effect; in fact, films from solutions swell more in water vapor than do films from latexes.

INTERPRETATION OF THE RESULTS

From the data presented above, it follows that rubber films prepared from latexes and from solutions differ radically from one another in a number of

TABLE 3
SWELLING OF FILMS IN WATER VAPOR

Material	Degree of swelling in percentage
Revertex	18.7
Natural-rubber solution	25.9
Igetex-S	18.7
Buna-S solution	21.9

properties, and that these differences appear to be quite independent of the nature of the polymer.

The complete absence or near absence of shrinkage of latex films indicates the absence of stresses during their formation, i.e., the absence of a restraining effect by such rigid supports as glass and cellophane on adjoining hydrophilic substances forming the outer layer of the globules.

During the formation of films from solutions, the restraining effect of these rigid supports is so much greater that it causes considerable stress and, accordingly, shrinkage of the films. The relatively much greater stresses which remain in films prepared from solutions in comparison with latex films are reflected in the results of measurements of stress relaxation (see Figure 2). Although in films of Revertex, the stress falls to 45 per cent of its original value in

2 hours, and in Igetex films, to 15 per cent, in films from solutions of the corresponding rubbers, it falls only to 72-50 per cent. It is possible that the stresses which are set up in films during their formation from solutions are caused by the comparatively low concentration of the solution. This question requires further study.

Radical differences between films prepared from latex and films prepared from solutions are evident in the residual elongation as well as in the tensile strength. The latter is much higher in the case of latex films. Incidentally, this fact indicates that, in the process of subsequent formation of films from solutions prepared from latex films, there is no appreciable oxidation of the polymer. On the contrary, in the case of films prepared from solutions, the residual elongations are considerably higher, especially in the case of natural rubber.

According to contemporary theories of the mechanism of formation of films of high-polymer substances⁸, the tensile strength of the latter must be proportionately higher, since the molecules of the polymer are more strongly oriented. The greater the stresses to which the films are subjected during their preparation, the higher is the degree of orientation. Such theories are correct in cases where the formation of films takes place at temperatures below the vitrification point, where the stresses which are set up in the films are not released, and where orientation of the molecules caused by these stresses is preserved.

In our experiments, the sheets were formed at a temperature above the vitrification point of the polymer, and, consequently, the difference between the properties of films from latex mixtures and from solutions cannot be explained in the manner indicated. It should be noted, however, that, under these conditions, unrelaxed stresses remain in films from solutions. The cause of these differences evidently lies in the different structure of films from solutions and from latexes and, in particular, in the role of the network of hydrophilic substances in the latexes.

During the formation of latex films, the lack of a fixing effect on the part of the support allows the globules to arrange themselves freely and comparatively loosely beside one another as the water evaporates, and then the outer layers, in contact with one another, form a network through the whole mass of the film. At a number of points the outer layer is broken, and there is a coalescence of the rubber content of the globules.

As a result of this process, a loose cellular structure is formed. When a film is stretched, it first becomes denser, owing to the disappearance of the separate cells and cavities, and the modulus then is small. At greater elongations (500 per cent), the modulus increases sharply and the stress-strain curve assumes a shape characteristic of a vulcanizate. The network of substances other than rubber behaves in this case like that of particles of active filler⁹, in that its presence causes an increase of tensile strength.

During the deformation of a latex film, the slipping of individual globules past one another is facilitated, and this leads to a large residual deformation and small residual stress during relaxation. At small deformations, such as those caused by swelling in water vapor, the network formed by the outer layer of the globules is strong, and limits the extent of the swelling.

During the solution of a latex film, the outer layers of the separate globules and the network are completely destroyed and hydrophilic substances in the form of separate fragments of the outer layers are embedded in the mass of the polymer. When such a system is deformed, its behavior is governed chiefly by

the properties of the polymer itself. This determines the form of the stress-strain curve characteristic of unvulcanized rubber.

The absence of a loose porous structure is one cause of the higher initial modulus, the lower the residual deformation, and the greater residual stress during relaxation. Since the nonrubber substances do not form a solid network in a film prepared from solution, they cannot function as an active filler, and the tensile strength of these films is lower than that of films prepared from latex. The absence of a solid network in the presence of the same concentration of hydrophilic substances leads to a higher swelling maximum in water vapor.

The greater swelling of films prepared from solutions in comparison with latex films may also be explained by the fact that, in the latter case, a part of the polar groups in the nonrubber outer layer of the globules, which govern the absorption of water, are screened by the polar groups of the outer films of neighboring globules. In films prepared from solution, the nonrubber substances are uniformly dispersed throughout the polymer, and no such screening can take place. At present, it is still impossible to give a definitive explanation of this phenomenon.

All these phenomena appear most evident in films of natural rubber. In the case of films prepared from Igetex and from Buna-S solutions, the differences between them are somewhat obscured, but shrinkage, differences of residual elongation, tensile strength, and behavior during swelling are quite pronounced. It is characteristic of butadiene-styrene rubber that films from solution have a higher modulus than that of latex films.

In the case of films of natural rubber, the contrary is observed. Furthermore, if the modulus of a film from a Buna-S solution, as would be expected, is less than that of a film from a natural-rubber solution, then the modulus of an Igetex film is higher than the modulus of a Revertex film.

In all probability this is explained by the fact that, in the case of Igetex films, the network of nonrubber substances has a very stiff structure. The presence of a stiff structure can also be a cause of some shrinkage of these films. An indirect confirmation of this is the formation of cracks during the preparation of Igetex sheets by pouring onto glass at room temperature, and the absence of cracks at high temperatures. An Igetex film evidently has a less porous structure than a Revertex film, and its structure does not change greatly during stretching. A consequence of this is its higher initial modulus and the lack of any further increase at high elongations, such as occurs with films prepared from natural latex.

In order to confirm the influence of the structure of a film on its mechanical properties, the following experiment was carried out. Revertex and Igetex films, prepared under the usual conditions (on cellophane at 50°) were swollen in benzene fumes for three days. These films were then reduced to their original weight in a vacuum.

TABLE 4
INFLUENCE OF REVERSIBLE SWELLING IN BENZENE VAPOR ON THE
MECHANICAL PROPERTIES OF LATEX FILMS

Material	Modulus at 100% (kg. per sq. cm.)	Residual elongation (%)
Revertex before milling	2.9	20
Revertex, after reversible swelling	5.1	10
Igetex, before swelling	4.7	15
Igetex, after reversible swelling	3.9	5

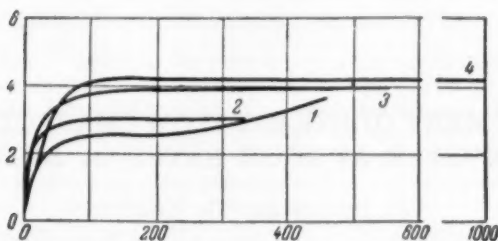


FIG. 3.—Stress-strain curves of films (a) from Revertex: 1. Before swelling. 2. After swelling in benzene vapor. (b) From Igetex: 3. Before swelling. 4. After swelling in benzene vapor. The abscissa indicates the elongation at rupture in percentage; the ordinate the tensile strength in kg. per sq. cm.

The mechanical properties of the films were determined both before and after reversible swelling. The results obtained are given in Table 4 and Figure 3. (Here the values for the original films are somewhat different from those represented in Table 1, because they were prepared from another batch of latex). The difference between the properties of the films before and after swelling in benzene fumes is very evident.

When a polymer swells, its original network is irreversibly destroyed, and this leads to a sharp change of mechanical properties and approximation of them to those of films prepared from solutions.

CONCLUSIONS

1. The mechanical properties, shrinkage, and swelling in water vapor of rubber films prepared from various latexes and rubber solutions, were studied.
2. It is shown that the behavior of films varies with the method of preparation.
3. An explanation of the difference in properties of rubber films prepared from solutions and from latex mixtures is suggested, based on the presence in films from latex of a network of nonrubber substances.

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MEASUREMENT OF STEADY FLOW CHARACTERISTICS OF RUBBER AT HIGH RATES OF SHEAR *

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INTRODUCTION

Various workers have measured the flow properties of rubber at shear rates from 10^{-6} to 10^3 sec^{-1} . Below a shear rate of 0.1, all the results give a linear relationship between log shear rate and log shear stress, but at higher shear rates there is curvature away from the log shear stress axis. Few measurements have been made at shear rates above 5 and, due to shear heating errors, the evidence produced is controvertible.

The apparatus to be described enables more accurate measurements to be taken at shear rates between 1 and 100 and the results obtained are compared with those obtained by other workers using different types of instruments.

APPARATUS

In the coaxial cylinder viscometer shown in Figure 1, the material is forced into the annular gap formed between an outer cylinder *A* (diameter 1.25 inches) and a rotor *B* by pressures up to 250 kg. per sq. cm. The gap at the lower end of the annulus is closed by a baseplate *C*, fastened to the outer cylinder. The baseplate hole is one to three-thousandths of an inch larger than the rotor and effectively prevents escape of the material under test while avoiding mechanical contact between the two parts.

The rotor speed is continuously variable from 1 to 60 r.p.m. The torque at the outer cylinder, which is carried on ball thrust and roller bearings, is measured by the deflection of a loaded pendulum.

To shorten the length of the annulus, the whole of the outer cylinder mounted on its bearings can be moved relative to the rotor on a screw thread *D*. This permits end corrections to be made quickly by taking readings at two or more positions. By unscrewing *D* completely, the outer cylinder can be removed for the insertion of different diameter or different length rotors and their associated baseplates. The rotor diameters available give annular gaps from 0.01 to 0.25 inch.

The outer cylinder is heated by six cartridge elements placed symmetrically in the body of the cylinder, while the rotor stem is heated by induction from a 1000 c/s supply. Temperature is measured by the insertion of thermocouple needles into the cylinder and rotor.

Pressure is maintained on the sample by force transmitted through a single ball to the plunger *E*. A double-acting air cylinder supplies the force and, by reversing the air supply, the plunger can be extracted from the cylinder.

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SPECIFIC FEATURES OF THE APPARATUS

The mechanical rigidity of the cylinder and rotor mounting enable uniform thin films to be sheared, while the high pressures which can be exerted by the plunger facilitate filling the annular gap. Shear heating and the variation of shear rate across the gap are small. The maximum permitted temperature rise due to shear heating was 5°C .

The reservoir above the rotor permits successive measurements to be made rapidly on new portions of the sample of material, which are introduced into the annulus by opening the bottom gap by lowering the outer cylinder.

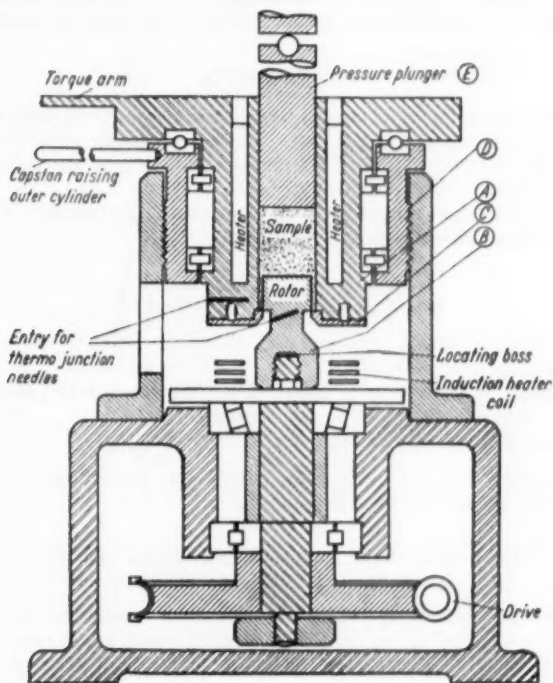


FIG. 1.—Coaxial cylinder viscometer.

The availability of a wide range of pressures (to 250 kg. per sq. cm.) permits evaluation of pressure coefficients.

PROCEDURE

The material is inserted in the cylinder when the temperature of the apparatus is within 2°C of that required, and the temperature is measured before and after each series of measurements. Pressure is applied and a sample is forced into the annulus.

The pressure is maintained steady during all readings on one material;

normally 60 kg. per sq. cm. is used for moderately hard rubbers, following determinations of the pressure above which the torque readings are independent of pressure change, indicating absence of slip.

The rubber close to the rotor attains uniform temperature in less than one minute, but that in the reservoir will take a considerable period to attain uniformity. This is unimportant, since tests show that the shear strain only extends a small way from the top of the rotor. When the rubber has attained the temperature, it is sheared at the highest rate to be subsequently used. After one minute rest, the measurements are made in turn from the highest to the lowest shear rates, with a one-minute rest period between each change of rate. Each reading is taken after shearing at a constant rate for one minute, and not more than six readings are taken without changing the material in the annulus.

CORRECTIONS

After the measurements have been made over the range of shear rates available by altering the speed of the rotor, end correction experiments are made before clearing the rubber from the annulus. The normal correction is in the range 15 to 25 per cent of the shear stress.

The correction for variation of shear rate is made graphically by adding to the shear stress an amount given by the term:

$$\frac{1}{n} \log [(a/b)^{2n} - 1] \frac{a}{2n(a-b)}$$

where a = radius of outer cylinder

b = radius of inner rotor

n = slope of log observed shear stress/log shear rate $[(aw)/(a-b)]$
curve at the point to be corrected

w = angular velocity of the rotor.

The correction amounts to from 3 to 20 per cent, according to the gap used. The full theory is given in an associated paper¹.

VARIATION OF SHEAR STRESS/STRAIN CURVES WITH TEMPERATURE

Figure 2 shows smoothed results on a sample of masticated natural rubber (Mooney 75) at temperatures from 90 to 150° C and a shear rate variation of 1 to 100. Individual results vary by approximately ± 3 per cent from these curves.

Groups of curves of very similar form are obtained when rubbers which have been subjected to a wide range of mastication treatment (Mooney values from 85 to 41) are tested over the same temperature range.

At a shear rate of one, there is a spread of results of shear stress. The more masticated materials and those tested at the higher temperatures give shear stresses of the order 5×10^5 dynes per sq. cm and the lower temperature and less masticated material of the order 10^6 dynes per sq. cm. At a shear rate of 100, however, all the results tend to the same value of the order 2.5×10^6 dynes per sq. cm., irrespective of testing temperature or mastication treatment over the ranges tested.

Below a temperature of 70° to 90° C, there is a marked change of the flow behavior of the material, resulting in stresses higher than the above limit and

in erratic readings² and lack of convergence (see Figure 2). Observations during the early period of milling masticated rubber show that high power consumption, tearing, roughness, and generally erratic flow behavior occur on the mill, and that smooth flow sets in relatively suddenly as the temperature of the materials reaches 60° to 90° C.

Although all isothermals in the temperature region 90° to 150° C converge to the same limit, they do not always do so uniformly. Similar non-uniform behavior is shown in results published by Mooney³ and by Whorlow⁴.

It appears that previous shear history and, hence, the test procedure can give rise to deviations in the observed results, so that time must be regarded as a parameter in defining the shear stress/shear strain relationship.

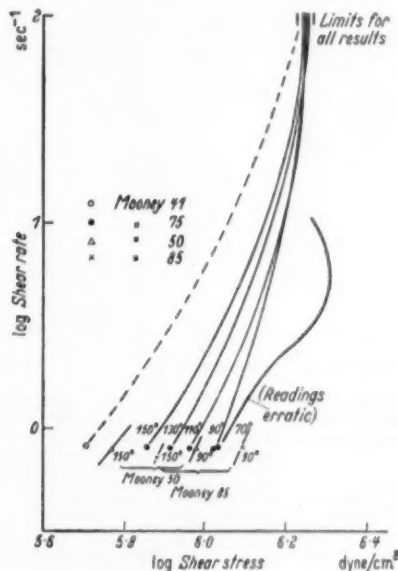


FIG. 2.—Variation of shear stress with temperature.

COMPARISON WITH OTHER RESULTS

The results obtained with this instrument are compared with those published by Saunders and Treloar², Mooney³, Whorlow⁴, Scott and Whorlow⁵ and Piper and Scott⁶ in Figures 3 and 4.

Figure 3 indicates the generalized flow characteristic from shear rates 10^{-6} to 100 and Figure 4 gives more complete results in the 1 to 100 shear rate region.

The authors' results for a shear rate 1 to 10 agree closely with those of other workers using corresponding rubbers, with the possible exception of the lower temperature results of Treloar². The values for factory-masticated rubber lie in the right-hand third of the graphs and approach a limit of shear stress. There is, however, no definite lower limit, the shear stress being reduced as test temperatures and milling treatment increase.

For shear rates 10 to 100, the authors' values for both hard and very soft

rubbers give a smooth continuation of the results published by other workers at lower shear rates.

The strong convergence above a shear rate of 10 to a stress limit of the order of 2.5×10^4 dynes per sq. cm. occurs over a wide temperature and molecular weight range for natural rubber.

A similar convergence to a similar limit value holds for Butyl rubber, but Neoprene, butadiene-styrene and butadiene-acrylonitrile rubbers show little, if any, convergence in the above shear rate range.

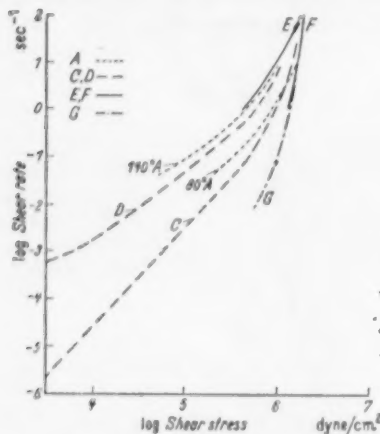


FIG. 3.—Generalized flow characteristic from shear rates 10^{-6} to 100.

A Saunders and Treloar
B Mooney
C Mooney
D Piper and Scott
E Bulgin and Wratten
F Bulgin and Wratten
G Whorlow
H Whorlow
I Whorlow

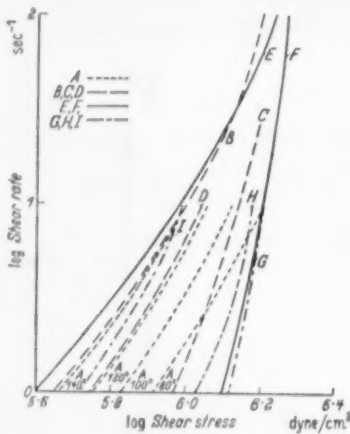


FIG. 4.—Flow characteristic from shear rate in range 1 to 100.

Biconical rotor, tested at 80° to 140° C.
Coaxial cylinder, tested at 140° C, milled 30 minutes.
Coaxial cylinder, tested at 100° C, milled 5 minutes.
Biconical rotor, tested at 100° C, milled 60 minutes.
Concentric cylinder 140° , soft rubber.
Concentric cylinder 100° , hard rubber.
Biconical rotor, 100° , milled 2 minutes.
Biconical rotor, 100° , milled 5 minutes.
Biconical rotor, 100° , milled 20 minutes.

SUMMARY

A coaxial cylinder viscometer suitable for use with long-chain polymers and technical rubberlike materials is described. Special features of the apparatus are the use of thin films to reduce heating, the ease of obtaining end corrections, and the use of high pressures to eliminate slip and facilitate filling the shearing gap. Results with uncompounded rubber show that the shear stress converges to a value of approximately 2.5 dynes per sq. cm. at shear rates in the region of 100, and that this value is independent of temperature (90° to 150° C) and of the chain length of the polymer. Certain polymers do not show this convergence.

ACKNOWLEDGMENTS

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BREAKAGE OF RUBBER-FILLER LINKAGES AND ENERGY DISSIPATION IN STRESSED RUBBER*

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INTRODUCTION

The modulus of rubber vulcanizates is dependent on the degree of cross-linking. A marked stiffening is observed if they are reinforced by colloidal fillers, but they can then be softened drastically by preextensions which exceed the extension of the rubber used to determine the modulus. This phenomenon was first studied and appreciated in some detail by Mullins¹ and is discussed quantitatively by the author and Parkinson². The following contribution is concerned almost exclusively with the weak-type (secondary) linkages which stiffen the rubber when fillers are present, and which may be readily broken by prestressing. The term primary linkages is here used to describe any linkages of a stronger type for which the filler may be responsible, together with the sulfur linkages normally present following the process of vulcanization.

GENERAL EXPERIMENTAL PROCEDURE

Experiments were carried out on a Goodbrand tensile testing machine, using ring-shaped test-pieces of external diameter 5.23 cm. and cross-section 0.4 by 0.38 cm. The rate of extension was 20 inches per minute, and the tests were carried out in a controlled atmosphere at 70° F ($\pm 2^\circ$) and 65 per cent humidity. Four successive stress-strain curves were recorded on the machine, the ultimate stress (i.e., the prestress) being the same in each case. The test-pieces were held at the ultimate stress for 30 seconds before the stress was released, but later the time was shortened to 15 seconds without appreciable effect.

In Figure 1, P, Q, and R are points corresponding to the ultimate extension on the previous curve. The difference between the area OAE and the area OPE is proportional to the difference in energies required to extend the rubber successively to the same elongation. The difference in energies for successive extensions has been used as a rough measure of the energy dissipated during the first extension in breaking linkages². It should not be confused with the difference in area under the extension and retraction curves, which includes the normal hysteresis loss when there is no softening. The energy lost in breaking linkages during the third extension, i.e., third prestress, is relatively small, and the sum for three consecutive prestresses S provides a rough measure of the energy H dissipated by prestressing in these experiments. Throughout this paper, an application of prestress S should be understood to mean three successive applications in the manner described, the resulting stress-strain properties being revealed by the fourth extension curve. Areas were measured by a planimeter and converted to calories H dissipated per cubic centimeter of test-piece.

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QUANTITATIVE DESCRIPTION AND INTERPRETATION OF STRESS-STRAIN BEHAVIOR

The softening of rubber compounds during extension is minimized by prestresses involving larger extensions. The relation between stress F (kg. cm.⁻² of cross-section before stretching) and extension ratio may then be described by an equation given by the author and Parkinson²:

$$\ln F - \phi(\alpha) = \ln G + \mu(\alpha - 1)^4 \quad (1)$$

α is the ratio of the extended to the initial length and the function $\phi(\alpha)$ depends only on the extension in accordance with the equation:

$$\phi(\alpha) = 0.31(\alpha - 1) + \ln 1.62[1 - (1/\alpha^2)] \quad (2)$$

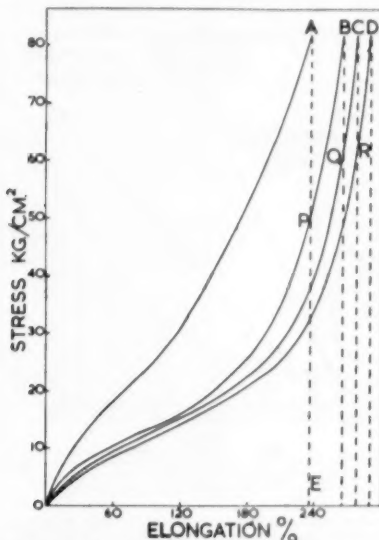


Fig. 1.—Stress-strain curves of carbon-reinforced rubber after successive prestresses of equal magnitude.

The parameters G and μ have been termed the modulus and extension factor, respectively, and both decrease as the prestress increases². Equation (1) applies for a wide range of extensions following prestressing, and it is particularly satisfactory if attention is confined to those between 70 and 400 per cent, though the upper limit may be set below 400 per cent by the prestress elongation.

Equation (1) was established for Hevea natural rubber², so that an application would be interesting in the case of the butadiene-styrene copolymer, Krylene, which does not crystallize at high extensions. Figure 2 records results obtained with Krylene synthetic rubber reinforced by HAF carbon black. This further success of the equation shows that it has wide applications. The compound formula (parts by weight) was: Krylene 100, HAF black 50, stearic acid 1, zinc oxide 3, accelerator (Santocure) 1, sulfur 1.75, and antioxidant 1, the vulcanization time being 200 minutes at 280° F.

The parameter G in the above equation has been used as a rough measure of the linkages that have survived prestressing, including the primary sulfur-linkages formed during the vulcanization process. The author is unable to provide a rigorous theoretical justification of this assumption, which corresponds to the simple kinetic theory expression of the effect of crosslinking, but G will clearly reflect changes in the number of rubber-filler linkages, and the practical value and success of the assumption as a working hypothesis are fully demonstrated. It has led to the development of a concept of force per linkage factor X due to prestressing, and the idea of a linkage strength factor as the value of X when breakage occurs². This involved the hypothesis that the concentration of filler effects the number of linkages, but not their strength. The quantity X was then defined as that function of the prestress S , corresponding extension ratio α , and corresponding or residual modulus G , which determines

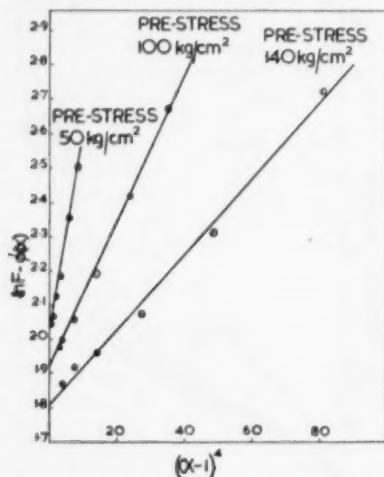


FIG. 2.—Application of Equation (1) to Krylene (GR-S) synthetic rubber containing HAF carbon black ($V = 0.26$).

the softening, and thus the strength of the strongest linkages broken, in conformity with the above hypothesis. With the aid of dimensional considerations, the function $X = \alpha S/G^{1/2}$ was obtained which satisfied this definition. In Hevea rubber containing colloidal fillers, the proportion of secondary linkages with strengths between X and $X + dX$ is then given by expression²:

$$dG/G_r = - (K^2 X^{1/4}) \exp\{-KX^{1/4}\} dX \quad (3)$$

This distribution is described by two parameters. One of them, G_r , is a measure of the total number of secondary linkages present before stress is applied; the other, K , describes their strength. The form of the distribution was determined empirically, using values of dG/dX obtained from the experimental data, and postulating distributions for trial which seemed broadly consistent with the experimental trends, and yet consistent with the assumption $dG = 0$ when $X = 0$. A rough plot of the distribution is shown in Figure 3 for $G_r = 4.0$ and $K = 0.276$ in order to illustrate the general shape of the curve. The ordinate

ΔG is a measure of the number of linkages having strengths in the range $X \pm 5$, values of $X \pm 5$ being plotted as abscissas. The initial part of the curve for $X < 10$ is beyond the range studied experimentally and so is not sanctioned by any experimental data. The law of softening expressed by the above distribution may be written²:

$$G = G^* + G_0 F(X) \quad (4)$$

$$F(X) = (K^3/4) \int_x^\infty X^{\frac{1}{2}} \exp\{-KX^{\frac{1}{2}}\} dX \quad (5)$$

where G^* is the residual modulus determined by strong-type (primary) linkages, including those due to vulcanization.

The preceding definition of X involves the hypothesis that K should be independent of the concentration of filler. Evidence that this is substantially in agreement with experiment is shown in Figure 4, where the modulus G is plotted

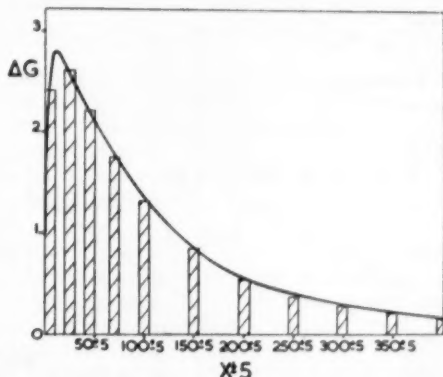


Fig. 3.—The distribution of strengths of the secondary filler-rubber linkages in terms of strength factors X .

against $F(X)$ for various volumes V of MPC channel black per unit volume of Hevea rubber, taking $K = 0.276$ in each case. The compound formula was (in parts by weight) Hevea rubber 100, MPC black (variable), stearic acid 2, zinc oxide 5, Santocure 0.8, sulfur 2.5, and antioxidant 1, the time of vulcanization being 65 minutes at 280° F. The prestresses ranged from 30 to 200 kg. per sq. cm. Evidence of a common linkage strength distribution parameter $K = 0.276$ for a variety of grades and types of filler in Hevea rubber has been presented by the author and Parkinson². There is also some indication that it may not be confined to fillers in Hevea rubber, as can be seen from Figure 5, which shows the graph of G vs. $F(X)$ for $V = 0.26$ volume of HAF black in Krylene synthetic rubber. With K fixed as 0.276 the quantity $F(X)$ is, therefore, uniquely determined by X , and may be obtained from graphs prepared to facilitate estimation for any value of X .

Vulcanizates without fillers show a relatively small degree of softening with prestressing, presumably because of the breakdown of some kind of intermolecular cohesion or other structural weakness which may be present. Therefore to assess more accurately the filler's component of the softening and energy dissipa-

tion of reinforced rubber, the relatively small estimates for the rubber matrix alone should be made, using the same mathematical form of expression as a useful, though not very accurate, approximation. This has been done for a typical unreinforced vulcanizate, later referred to as vulcanizate B, and otherwise similar to the reinforced compounds, having the formula: rubber 100, stearic acid 2, zinc oxide 5, Santocure 0.5, sulfur 2.5, and being vulcanized for 55 minutes at 280° F. This has indicated that a component of G , for reinforced vulcanizates amounting to about $b = 0.9$ should be allowed roughly to account for the softening of the rubber matrix itself. An unreinforced compound A, containing 8 per cent by weight of sulfur only, and vulcanized for 3 hours at 297° F without accelerator and zinc oxide, was less affected by prestressing, the corresponding values of b being 0.3.

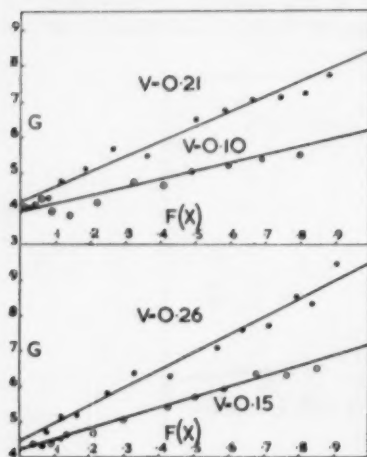


FIG. 4.—Relation between modulus G and $F(X)$ for several concentrations of MPC channel black in Hevea rubber.

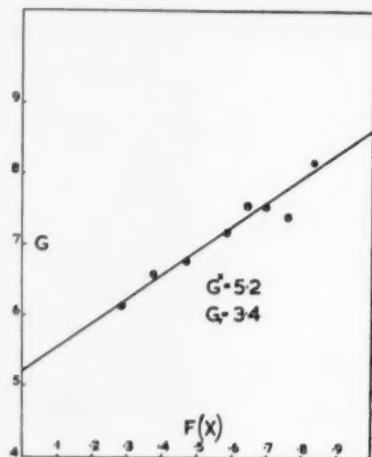


FIG. 5.—Relation between modulus G and $F(X)$ for HAF black in Krylene (GR-S) synthetic rubber.

The foregoing analysis of stress-strain behavior in terms of linkage formation by fillers may be criticized because it takes no account of the volume occupied by the filler. In the kinetic theory of rubber elasticity, the modulus is directly proportional to the absolute temperature and to the number of rubber chains per unit volume. This indicates that the effect of dilution of the rubber by filler is to reduce the number of chains and, therefore, the modulus in the ratio $1:1 + V$. The corrected modulus is, therefore, $(1 + V)G$. On the other hand, the quantity X is independent of the correction for the volume occupied by the filler. This can be seen by considering a unit cube of rubber whose dimensions have been increased in the ratio $(1 + V)^{1/3}$ by incorporating volume V of filler. The force applied to this cube to give prestress S is therefore $(1 + V)^{1/3}S$, and the corrected modulus $(1 + V)G$ is a measure of the number of linkages in the cube. The corrected value of X is, therefore, as before:

$$X = \alpha(1 + V)^{1/3}S / (1 + V)^{1/3}G = \alpha S / G$$

The need to multiply values of G^* and G_r by $1 + V$ explains why uncorrected values of G^* for rubber containing 26 parts by volume of calcium silicate (Silene) or magnesium carbonate (see reference 2, table XII, p. 810) are considerably less than for unloaded vulcanizates. Such a reduction in G^* will occur with fillers which do not introduce a strong type of linkage and so do not add to the primary linkages formed by sulfur. The correction places even more emphasis on the significance of the increase in primary linkages observed with colloidal fillers such as HAF and MPC blacks². This topic, however, and more general aspects of the phenomenon of reinforcement are mainly outside the scope of this paper.

CALCULATION OF ENERGY DISSIPATED FROM DISTRIBUTION OF LINKAGE STRENGTHS

Using the modulus G as a measure of the linkages, and applying the volume correction to Equation (3), it can be seen that the secondary linkages, $-(1 + V)dG$, with strength factors between X and $X + dX$ are given by the equation:

$$-(1 + V)dG = [K^2(1 + V)/4]G_r X^{\frac{1}{2}} \exp\{-KX^{\frac{1}{2}}\} dX \quad (3a)$$

Now consider the mechanical energy dissipated in breaking linkages as an alternative method of describing their strength, and let this energy E correspond to strength factor X . A definite correspondence between the two measures of linkage strength is consistent with any relationship between them which does not involve the variables of prestressing. In the following calculations, the simplest possible case is taken with E directly proportional to X so that:

$$E = \eta X \quad (6)$$

where E is expressed in calories per unit change in modulus and η is the corresponding constant of proportionality. The number of linkages with strength factors between X and $X + dX$ and, hence, energies of breakage between E and $E + dE$ calories per unit change in modulus is $-(1 + V)dG$ in accordance with Equation (3a). The energy dissipated per unit volume of rubber in breaking these particular linkages is, therefore, $-(1 + V)EdG$; and on applying prestress S the energy dissipated per cubic centimeter of rubber in breaking all the linkages with energies of breakage between 0 and E is:

$$(1 + V)H = -(1 + V) \int_0^E EdG \quad (7)$$

where H is the energy dissipated per cubic centimeter of rubber and filler. Substituting Equations (3a) and (6) in the above integration, we obtain:

$$(1 + V)H = [\eta K^2(1 + V)/4]G_r \int_0^E X^{\frac{1}{2}} \exp\{-KX^{\frac{1}{2}}\} dX \quad (8)$$

The solution of this integral is:

$$-\frac{12\eta(1 + V)}{K^2} G_r \left[\left(1 + KX^{\frac{1}{2}} + \frac{K^2 X}{3} + \frac{K^3 X^{\frac{3}{2}}}{6} + \frac{K^4 X^2}{24} \right) \exp\{-KX^{\frac{1}{2}}\} \right]_0^X$$

and with $\Omega(X)$ an appropriate function of X , Equation (8) becomes:

$$(1 + V)H = \eta(1 + V)G_r \Omega(X) \quad (9)$$

or:

$$H = \eta G_r \Omega(X) \quad (10)$$

Since K is constant and equal to 0.276 the function $\Omega(X)$ is uniquely determined by X and can be graphed in the same manner as $F(X)$ to facilitate evaluation for any value of X and for any compound. It has the value:

$$\Omega(X) = \frac{12}{K^2} - \frac{12}{K^2} \left[1 + KX^{\frac{1}{2}} + \frac{K^2 X}{2} + \frac{K^3 X^{\frac{3}{2}}}{6} + \frac{K^4 X^2}{24} \right] \exp\{-KX^{\frac{1}{2}}\} \quad (11)$$

$$= \frac{12}{K^2} [1 - F(X)] - X[F(X) + (KX^{\frac{1}{2}} - 1) \exp\{-KX^{\frac{1}{2}}\}] \quad (12)$$

The latter form of expression was most convenient as provision for evaluating $F(X)$ had already been made.

To take account of the component of the softening and energy dissipation which is not due to the filler, an attempt should be made to provide at least a rough evaluation of $H/\Omega(X) = a$ and $G_r = b$ for the vulcanizates without filler, and also $\eta_0 = a/b$. The value of η relating strength factors of the filler linkages with energies of breakage can then be calculated from Equation (9) by taking the above components contributed by the rubber alone and subtracting them respectively from:

$$(1 + V) \frac{H}{\Omega(X)} \text{ and } (1 + V)G_r$$

for the loaded rubber in order to obtain the components representing only linkages introduced by the filler. The value of η for rubber-filler linkages is then given by:

$$\eta = \frac{(1 + V) \frac{H}{\Omega(X)} - a}{(1 + V)G_r - b} \quad (13)$$

Since G_r may be obtained by applying Equation (4) to the stress-strain curves, and since the energies may be determined roughly by experiment in the manner described earlier, it is possible to calculate η and express linkage strength factors X as energies of breakage E by multiplying by η .

APPLICATION OF ENERGY CALCULATIONS TO EXPERIMENTAL DATA

VULCANIZATES WITHOUT COLLOIDAL FILLERS ($V = 0$)

Experimental results obtained for the energy $(1 + V)H = H$ dissipated per unit volume of rubber by various prestresses are recorded in Table I for the unaccelerated vulcanizate A and the accelerated vulcanizate B. Vulcanizates without colloidal fillers have relatively large X values for a given prestress because of their low modulus and the high extension which accompanies the prestress. For this reason, prestresses between 10 and 30 kg. cm.⁻² were included to obtain some low X values.

In Figure 6, the energy dissipated is plotted against $\Omega(X)$ and a rough value for the slope $H/\Omega(X)$ of the graph may be quoted which, to some extent, represents data in the range $\Omega(X) = 0$ to $\Omega(X) = 100$. Figures 7 and 10 show that a tendency to upward curvature of the graphs is obtained also with the much larger energy dissipation of rubber containing fillers. Consequently it is probable that the deviation from linearity shown in Figure 6 is due only partially to error in attempting to apply Equation (9) to unreinforced rubber in particular,

TABLE I
STRESS-STRAIN DATA FOR UNREINFORCED HEVEA VULCANIZATES

Prestress, (kg./cm. ²)	Elongation % at prestress	Energy H (cal. per cc.)	X	$\Omega(X)$
Compound A				
10	181	0.012	11.8	0.6
15	289	0.013	24.6	1.9
20	373	0.050	40.1	5.0
30	479	0.073	74.2	14.6
40	545	0.22	110	26.0
50	599	0.29	143	37.2
60	643	0.65	185	52.5
80	720	1.07	288	78.6
90	746	1.30	330	88.5
100	782	1.75	397	101
Compound B				
10	125	0.013	8.3	0.4
20	306	0.072	30.0	2.6
30	438	0.19	61.8	10.6
40	502	0.44	90.5	19.6
50	552	0.61	121	30.0
60	586	0.89	157	42.0
80	641	1.70	247	66.3
100	688	2.44	328	88.3
120	721	2.97	416	104
140	748	3.95	497	116

although this did mean assuming the distribution of linkage strength factors to be the same as for linkages introduced by fillers. On the other hand, since Equation (9) also assumes the simplest possible relationship (Equation 6) between energies of breakage E and strength factors X , it is not surprising to find that the graphs are not perfectly linear. By trying more complex relationships between E and X , it would doubtless be possible to obtain a generally more accurate representation of the data for rubber, with and without fillers, but this has not been attempted here.

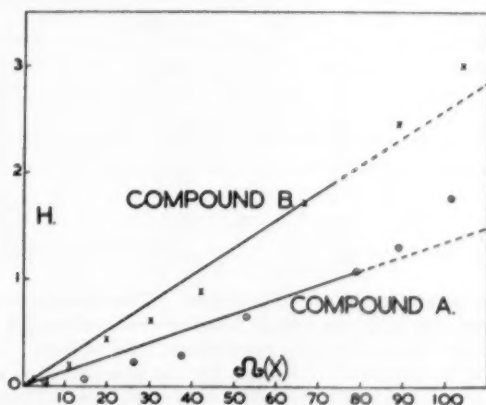


Fig. 6.—Relation between $\Omega(X)$ and the energy H dissipated per cubic centimeter of rubber in softening unreinforced vulcanizates by prestressing.

The approximate representation of the behavior of the accelerated vulcanizate by $H/\Omega(X) = a = 0.026$ for $V = 0$ and $f(X) = 0$ to 100 may be regarded as roughly that component of $(1 + V)H/\Omega(X)$ for reinforced rubber which is contributed by the rubber independently of the filler. Here H is understood to be expressed in calories per cubic centimeter of test-piece, which, in the absence of filler, has been taken to equal calories per cubic centimeter of rubber

TABLE II
STRESS-STRAIN DATA FOR VARIOUS CONCENTRATIONS OF MPC
BLACK IN HEVEA VULCANIZATES

Prestress (kg./cm. ²)	X	V = 0.052 $\Omega(X)$	(1 + V)H	X	V = 0.104 $\Omega(X)$	(1 + V)H
30	44	6.0	0.20	32	3.0	0.23
40	70	13.9	0.43	50	7.7	0.50
50	98	22.1	0.73	70	13.2	0.69
60	130	33.2	1.02	96	21.8	1.04
70	165	45.3	1.51	124	31.2	1.51
80	201	54.1	1.89	157	42.4	2.03
100	273	74.0	2.77	230	61.5	3.12
120	353	93.5	3.75	304	83.0	4.36
140	436	107	4.98	393	100	5.94
160	524	120	6.01	475	113	7.72
180	619	131	7.30	567	125	8.21
200	708	138	8.61	656	135	9.34

Prestress (kg./cm. ²)	X	V = 0.156 $\Omega(X)$	(1 + V)H	X	V = 0.208 $\Omega(X)$	(1 + V)H
30	24	1.8	0.15	19	1.2	0.20
40	37	4.3	0.36	29	2.5	0.43
50	53	8.2	0.63	42	5.4	0.60
60	72	13.9	0.99	56	9.2	0.90
70	93	20.9	1.50	73	14.2	1.19
80	118	29.0	2.09	93	20.9	1.65
100	177	48.1	2.98	144	37.8	2.83
120	236	63.0	4.12	199	53.7	4.18
140	310	84.4	5.39	259	70.1	5.11
160	388	99.4	7.30	344	91.8	7.23
180	468	112	9.09	417	104	8.32
200	552	123	10.3	519	119	10.4

Prestress (kg./cm. ²)	X	V = 0.260 $\Omega(X)$	(1 + V)H
40	25	2.0	0.46
50	33	3.2	0.59
60	47	6.6	0.97
70	61	10.4	1.27
80	77	15.7	1.65
100	117	28.4	2.73
120	159	42.9	3.87
140	214	57.6	5.27
160	284	77.6	7.33
180	348	92.5	8.60
200	426	105	10.2

with sufficient accuracy for practical purposes. The attempt to represent the secondary linkages initially present in unreinforced rubber by $G_r = b$ gives roughly $b = 0.9$ for the accelerated vulcanizate. By writing $V = 0$ in Equation (9), $\eta_0 = 0.03$ is obtained. Similarly for the unaccelerated vulcanizate A, we have $H/\Omega(X) = 0.013$ and $G_r = 0.3$, so that $\eta_0 = 0.04$. There is, of course, no justification for concluding that there is a real difference between the η_0 values of compounds type A and B on this evidence.

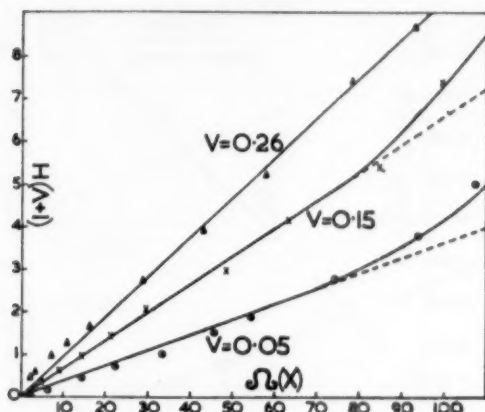


FIG. 7.—Relation between $\Omega(X)$ and the energy $(1 + V)H$ dissipated per cubic centimeter of rubber in softening vulcanizates containing various concentrations of MPC black.

VULCANIZATES CONTAINING COLLOIDAL FILLERS

Estimates of energy dissipated were obtained from the stress-strain data used to plot Figure 4, which represents part of an experiment with compounds having 10, 20, 30, 40, and 50 parts by weight of MPC black on 100 parts of Hevea rubber. Data for these compounds are shown in Table II.

According to Equation (9), the energy dissipated $(1 + V)H$ should be proportional to $\Omega(X)$. Figure 7 shows typical graphs for the vulcanizates with 10, 30, and 50 parts by weight of channel black. These are roughly consistent with the equation for values of $\Omega(X)$ between 0 and 100, but they show the tendency to upward curvature noted and discussed earlier in this paper. Values of $(1 + V)H/\Omega(X)$ were obtained from the slopes of the graphs which give a fair representation of data in the range $\Omega(X) = 0$ to $\Omega(X) = 100$. This corresponds to a wide range of prestresses. Thus for 10 and 50 parts loading, in this case $\Omega(X) = 100$ corresponds, respectively, with prestresses in the region 140 kg. cm.⁻² and 200 kg. cm.⁻² and $\Omega(X) = 10$ roughly with 35 and 70 kg. cm.⁻². Table III records values of $(1 + V)H/\Omega(X)$, and in Figure 8 these estimates, less the component $a = 0.026$ present independently of the filler, have been plotted against that volume V of filler per unit volume of rubber. The component of $(1 + V)H/\Omega(X)$ due to the filler is directly proportional to V in this case.

TABLE III
STRESS-STRAIN DATA FOR VARIOUS CONCENTRATIONS OF MPC BLACK
IN HEVEA VULCANIZATES

Parts by weight of carbon black on 100 of rubber	V	$(1 + V)H/\Omega(X)$	G_r	$(1 + V)G_r$
10	0.052	0.036	1.1	1.2
20	0.104	0.051	2.2	2.4
30	0.156	0.065	2.9	3.4
40	0.208	0.076	4.2	5.1
50	0.260	0.093	4.8	6.0

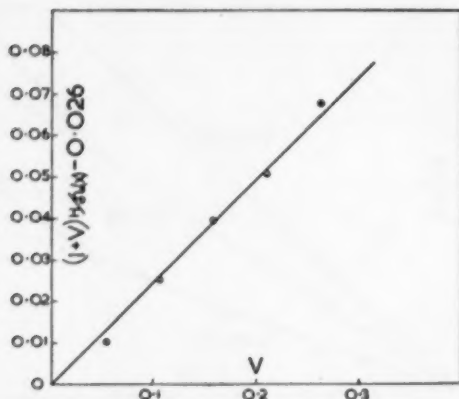


FIG. 8.—Effect of the concentration of MPC black on the component of $(1 + V)H/\Omega(X)$ due to breakage of the rubber-filler linkages.

Theoretically, $(1 + V)H/\Omega(X) - a$ may be plotted against $(1 + V)G_r - b$ for various loadings of filler to give a straight line which passes through the origin and whose slope is a mean value of η in accordance with Equation (13). This assumes that η for the linkages introduced by fillers is independent of the concentration of filler. Figure 9 shows the graph obtained with the MPC compounds studied if we take $a = 0.026$ and $b = 0.9$. This provides an estimate $\eta = 0.014$ for linkages introduced by MPC black, which is about one-half of the estimate $\eta_0 = 0.03$ for the few breakable linkages present without filler.

The above methods of studying the energy dissipated by prestressing have been applied to the stress-strain curves obtained with some vulcanizates whose behavior in some other respects has been discussed by the author and Parkinson². These were a "heat-treated" compound containing MPC black, and

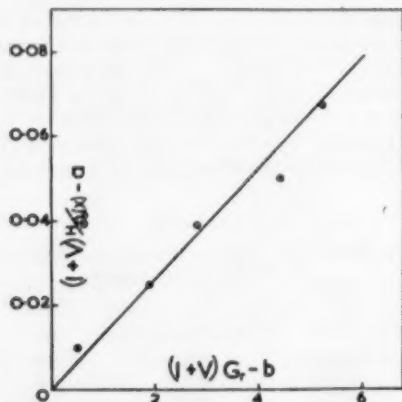


FIG. 9.—Effect of the secondary rubber-filler linkages at various concentrations of MPC black on the component of $(1 + V)H/\Omega(X)$ due to breaking them.

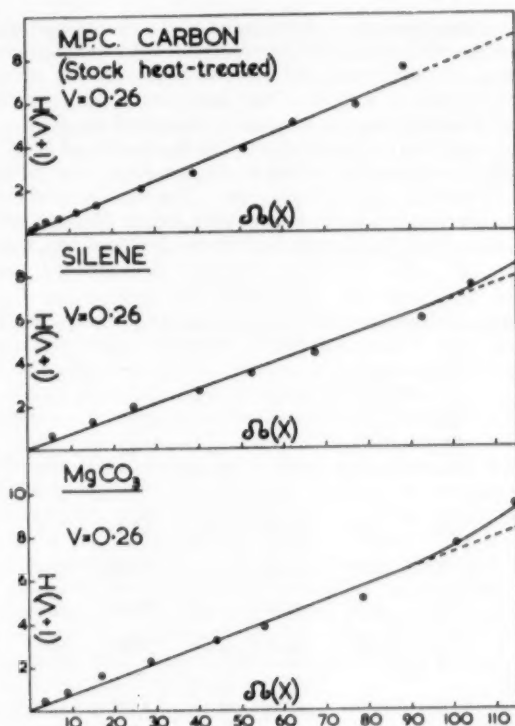


Fig. 10.—Relation between $\Omega(X)$ and the energy $(1 + V)H$ dissipated per cubic centimeter of rubber in softening various rubber compounds.

compounds containing, respectively, Silene (calcium silicate) and magnesium carbonate, each with 26 parts by volume of filler. Figure 10 shows graphs of $(1 + V)H$ vs. $\Omega(X)$, and Table IV records some other relevant results and values of η calculated from Equation (13). This application shows that the general procedure of analysis and calculations may be applied with some success in these cases also. Values of η obtained in all the experiments will be discussed later.

These studies have been extended by examining stress-strain curves obtained in a much wider investigation designed to compare other aspects of the behavior of colloidal carbons in rubber, including especially the evaluation of

TABLE IV
STRESS-STRAIN DATA FOR VARIOUS HEVEA VULCANIZATES CONTAINING
FILLERS ($V = 0.26$)

Type of filler and compound	G_r	$(1 + V)G_r$	$(1 + V)H/\Omega(X)$	η
MPC black (heat-treated compound)	2.6	3.3	0.077	0.021
Silene	2.2	2.8	0.068	0.022
Magnesium carbonate	3.4	4.3	0.072	0.014

G^* and G_r for various types of carbon black. Only the estimates of energy dissipated and values of G_r and $\Omega(X)$ (necessary for the calculation of η) will be considered here. In each case the volume concentration of filler per unit volume of rubber was $V = 0.26$. The compounds were vulcanized for 55 minutes at 280° F, and contained 0.5 part by weight of accelerator (Santocure), with the exception of those reinforced by calcium silicate and MPC (Spheron-6), HPC (Spheron-4), conductive channel (Spheron-C), and Graphon carbon blacks, which all had 0.7 part of Santocure. The remainder of the formula was Hevea rubber 100, stearic acid 2, zinc oxide 5, sulfur 2.5, and antioxidant 1.0. The value of $(1 + V)H/\Omega(X)$ was worked out for prestress 140 kg. cm.⁻² in

TABLE V
STRESS-STRAIN DATA FOR HEVEA VULCANIZATES CONTAINING VARIOUS
FILLERS ($V = 0.26$)

Type of filler	Mean particle diam. (m μ)	% elon- gation at pre- stress $S = 140$, (kg./cm. ²)	$\Omega(X)$	H_r cal./cc.	$(1 + V) \frac{H}{\Omega(X)}$	G_r	$(1 + V) \frac{H}{G_r}$	η
Conductive channel black (Spheron-C)	23	500	86.7	4.94	0.072	3.26	4.1	0.014
HPC black (Spheron-4)	24	430	69.6	4.46	0.081	3.85	4.9	0.014
MPC black (Spheron-6)	25	430	67.6	4.33	0.081	3.56	4.5	0.015
HAF black (Vulcan-3)	27	380	56.2	3.68	0.083	3.83	4.8	0.014
Graphitized channel black (Graphon)	25	680	113	4.45	0.050	2.05	2.6	0.014
FF black (Sterling-105)	32	450	74.7	4.70	0.079	4.37	5.5	0.012
FF black (Sterling-99)	39	460	73.2	4.72	0.082	3.46	4.4	0.016
Shawinigan acetylene black	40	360	50.0	3.90	0.097	6.19	7.8	0.010
SRF black (Sterling-S)	80	450	69.9	4.34	0.078	3.86	4.9	0.013
Lampblack	100	430	64.8	4.81	0.095	5.16	6.5	0.012
Calcium silicate	30	770	125	6.17	0.062	3.05	3.8	0.012

every case from stress-strain curves for two test pieces. Some typical estimates of the mean particle diameters of the filler are also shown in Table V to give an idea of the marked differences between them. The values of η shown in the table have been calculated, taking $a = 0.026$ and $b = 0.9$.

DISCUSSION

ANALYSIS OF SOFTENING AND ENERGY DISSIPATION

The foregoing pages have described the stiffening of rubber vulcanizates by incorporating colloidal fillers and how their softening by prestressing may then be analyzed and interpreted in terms of a distribution of strengths of secondary linkages formed by the filler in rubber. This interpretation of rubber softening

in terms of linkage strength factors has been further strengthened by the establishment of an approximate relationship between strength factors X and energies of breakage E . Thus, at low prestresses, a comparatively large number of linkages are broken with low X , but little energy is dissipated for a given change of modulus. At high prestresses, on the other hand, there is little further change of modulus, but much stronger secondary linkages with high energies of breakage are involved, and considerable energy is dissipated in breaking only a small number of such linkages.

It might be thought that the stiffest compounds with the greatest number of breakable linkages would dissipate the most energy on application of a fixed prestress, but this is not the case (see Table V). For instance, the calcium silicate and Graphon compounds have very high extension ratios α and low residual G for the fixed prestress, and this leads to high values of X and hence of $\Omega(X)$. Consequently, although these compounds have fewer secondary linkages, the 140 kg. per sq. cm. prestress involves higher force per linkage factors X , so that much stronger linkages are included among those broken, and the dissipation of energy is correspondingly large with Graphon and exceptionally large with calcium silicate. These results are brought substantially into line with those for the other fillers when the range of strengths of the broken linkages is taken into account by dividing the energies by $\Omega(X)$, and when allowance is also made for the total number of secondary linkages by substituting for $(1 + V)G$, in Equation (13) to obtain η . The high prestress extensions and abnormal energy dissipation of the Graphon and calcium silicate compounds are associated with much less stiffening by primary linkages G^* . A proper discussion of G^* values is, however, outside the scope of this paper, and they have been omitted from Table V. The dissipation of energy in reinforced rubber on stressing is evidently a complex study in which the concept of linkage strength factors X is of great value.

The calculated values of η in Table V are roughly similar for all the fillers without large deviation from the over-all mean of 0.013, which is practically identical with the average given earlier in this paper for several concentrations of MPC black. More work would be required to justify an attempt to discuss differences between the compounds. The estimates in Table IV for a heat-treated MPC black compound and a Silene (calcium silicate) compound are, therefore, considerably larger than all the other estimates so far obtained for fillers. The apparent difference in behavior would require further study for it to be accepted and explained, particularly as the calcium silicate filler represented in Table V shows no such difference, although Silene consists of particles of calcium silicate.

MECHANISM OF THE DISTRIBUTION OF SECONDARY LINKAGE STRENGTHS

The range of strengths of the secondary linkages due to fillers may be expressed in terms of strength factors by one distribution parameter K common to widely different rubber compounds. It has been shown that these strength factors X may be roughly converted to energies of breakage E in calories per unit change of modulus by multiplying by η . Experiments with a considerable number of fillers of various types have shown that η for linkages introduced by fillers can generally be taken to be 0.013, without much error, though there may be exceptions. This is about one-half the rough estimate $\eta_0 = 0.03$ made earlier for the secondary linkages which are apparently present to a small degree in vulcanizates without reinforcing fillers. Table VI shows the values of

E which correspond roughly with various values of X when η has the above values.

To obtain a rough appreciation of the significance of energies of this order of magnitude, let us consider the intermolecular cohesions or other readily breakable structures in unreinforced vulcanizates as simple linkages equivalent to those postulated in the kinetic theory of rubber elasticity. The modulus may then be taken to be roughly $\beta k T U$, where U is the number of linkages per unit volume, k is Boltzmann's constant, T is the absolute temperature, and β is a constant which is theoretically unity in an ideal case but larger in practice⁴. Consider one linkage with energy of breakage E calories per unit change in modulus, i.e., $\beta k T E$ per linkage, and suppose that this linkage involves x of the chemical groups in a long chain polymer molecule. Taking Avogadro's number to be 6×10^{23} , the energy of breakage per group is $(6\beta k T E/x) \times 10^{20}$ kcal. per mole. Even if an element of polar attraction is involved, it appears safe to

TABLE VI
CORRESPONDENCE BETWEEN LINKAGE STRENGTH FACTORS AND ENERGIES
OF BREAKAGE

X	Energy of breakage E in calories per unit change in modulus	
	$\eta = 0.013$	$\eta_0 = 0.03$
20	0.3	0.6
100	1.3	3.0
200	2.6	6.0
300	3.9	9.0
400	5.2	12.0
500	6.5	15.0

assume that the average energy of breakage per group will not exceed 10 kcal. per mole so that:

$$(6\beta k T E/x) < 10^{-19}$$

Since $\beta > 1$, a strong secondary linkage, with $E = 10$ calories per unit change of modulus, must involve at least 30 groups of a rubber molecule. By the same calculation a very weak linkage with $E = 0.5$ must involve at least one group (which, of course, is also the condition for the existence of a linkage). For purely van der Waals forces the energy of breakage would not exceed 4 kcal. per mole, and for $E = 0.5$ and $E = 10$ calories per unit change of modulus, the minimum number of groups involved in this case would be, respectively, 4 and 75.

In connection with the above results, it is noteworthy that physical linkages between molecules with participation of a considerable number of cohering groups in each linkage would help to account for the degree of elasticity shown by raw rubber before it has been masticated and vulcanized. In this discussion the main interest is the linkages introduced by fillers, and in the light of the above calculation it is evident from the order of magnitude of E for the strongest secondary linkages that these must be formed by physical attachments between rubber and filler which involve a number of chemical groups in the long chain polymer molecules. Differences in the number of adsorbed groups of molecules which have become attached to filler particles could, therefore, account for most of the distribution of strengths of the secondary linkages. This suggests that, as linkages of progressively lower strength are considered,

their numbers might drop sharply for strengths in the region corresponding to only a few attached groups, i.e., when it is difficult to find linkages which are weaker because they involve even fewer groups. Such an interpretation appears consistent with the form of expression represented in Figure 3, which describes the distribution of linkage strengths in accordance with Equation (3).

RELATION OF THE ABOVE STUDIES TO THE GENERAL PROBLEM OF REINFORCEMENT

Table V shows that the particle diameter of the filler has little or no importance in determining either the secondary linkages G_r or the energy dissipated in breaking them; yet it is a major factor in reinforcement, judged by tensile strength, tearing, and abrasion. It is also evident that considerations of secondary linkages in conjunction with particle diameter show no prospect of explaining the differences in reinforcing action between types and grades of filler. Such a conclusion is in accord with the emphasis placed by the author and Parkinson² on evidence that carbon blacks are responsible for some form of strong-type (primary) linkage formation in rubber. This aspect of the problem is not within the scope of the present contribution, but there is one important point which ought to be raised on the basis of the work considered here. It is that an appreciation of the presence of primary as well as secondary linkages due to the carbon black is apparently necessary even to understand the wide differences between fillers in the energy dissipated on breaking secondary linkages by a fixed prestress. The two types of linkage have opposed effects in this case for, whereas the energy dissipated by a fixed prestress increases with the number of secondary linkages present, it diminishes markedly with increasing numbers of primary linkages (which do not contribute to the energy dissipated by themselves breaking with the stress). For instance, between calcium silicate and the carbon fillers in Table V there is a major difference in the extension at the prestress and the energy dissipated relative to the secondary linkages available for breaking. Discussion of other evidence concerning primary linkages, their nature, and relation to reinforcement is beyond the scope of this paper.

CONCLUSIONS

The marked softening of reinforced rubber by applied stress can be interpreted in terms of a range of strengths of secondary linkages formed by rubber-filler attachments, and this can be described by one common distribution parameter K for several grades and types of filler in natural rubber, and also for at least one type of carbon black in Krylene (GR-S) synthetic rubber. Linkages of this type are of little significance in reinforcement, judged by tensile strength or abrasion resistance. The fact that the filler particle diameter had no influence in these experiments on the energy dissipated in breaking secondary linkages, or their number as reflected by their stiffening action, may be considered a serious objection to the presumption that specific surface or interfacial area determines linkage formation in rubber and, hence (supposedly), the reinforcement. There is evidence of primary (strong) linkages introduced by carbon blacks, and these are likely to have a more important role in determining the breaking, tearing, and abrasion of rubber.

SYNOPSIS

The stress-strain behavior of reinforced rubber is discussed in respect of the softening with applied stress and accompanying dissipation of energy. The

concept of linkage strength factors X for attachments between rubber molecules and filler particles is shown to have wide application and usefulness, and to be related to the energy dissipated in breaking the linkages. The strength factors are a function of the prestress when the linkages break, and also the corresponding extension ratio and residual stiffness; and for a variety of fillers and considerable range of values they can be roughly converted to energies of breakage in calories per unit change in modulus by multiplying by $\eta = 0.013$. The range of strengths of these secondary linkages due to fillers may be expressed in terms of X by one distribution parameter K common to widely different rubber compounds. Energy data suggest that they are formed by physical attachments involving a number of chemical groups in the long chain polymer molecules. Presumably the strength distribution is mainly due to differences in the number of groups involved. The particle diameter of the filler has little or no importance in determining the energy dissipated in breaking secondary linkages, or their number as judged by stiffening action; yet it is a major factor in reinforcement as judged by tensile strength, tearing, and abrasion. Considerations of secondary linkages in conjunction with particle diameter show no prospect of explaining the differences in reinforcing action between types and grades of filler. An appreciation of the presence of some form of strong-type (primary) linkages due to carbon black is apparently necessary to understand the wide differences between fillers in the energy dissipated on breaking secondary linkages by a fixed prestress.

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LOW-TEMPERATURE PROPERTIES OF PLASTICIZED BUTADIENE-STYRENE COPOLYMERS *

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INTRODUCTION

It is frequently desirable to subject high molecular-weight polymers to uses which require serviceability over a wide temperature range. In the case of elastomers, there is a limiting temperature below which they lose their soft pliable nature and become brittle and nonextensible. The temperature at which the change takes place is often called the second-order transition temperature or glassy state temperature, and is designated by the symbol, t_g . It has been pointed out¹ that it should be called the "apparent second-order transition temperature", since the experimentally determined values are somewhat time dependent.

This apparent second-order transition temperature has been characterized as an isoviscous², an isoelectric³, or an iso-volume state⁴, while Alfrey, Goldfinger, and Mark¹ interpret it as the temperature at which the diffusion of holes to the surface of a specimen acquires a rate comparable to the experimental time scale of the measurements. Buchdahl and Neilsen⁵, after consideration of the phenomena which could lead to a transition, concluded that, although a time effect does exist, the transition can only be due to the onset of rotations of chain segments. This explanation for the transition was first put forth by Alfrey and Mark⁶ and by Tuckett⁷, and is now widely accepted.

The effect of molecular structure on the apparent second-order transition temperature is readily seen by consideration of a few typical values. The value for natural rubber occurs at about -73°C . That for polystyrene varies somewhat with the investigator, but the best value seems to be about $+81^\circ\text{C}$. That for a 79/21 copolymer of butadiene and styrene is about -60°C . The value for emulsion polymerized polybutadiene is about -85°C , while that for sodium-polymerized material is about -50°C , and varies appreciably with the temperature of polymerization. The major structural difference between the two types of polybutadiene is the greater percentage of the monomer units in the 1,2-configuration in the sodium-polymerized material.

It has been common practice in the plastics field to incorporate certain plasticizers into polymers to make them pliable at room temperature. The effect has been shown to be lowering of the second-order transition temperature⁸. Tuckett⁷ suggested that swelling agents and plasticizers should reduce hindrance to rotation and hence decrease t_g . Wall and Miller⁹ argue that the swelling agent is made up of small molecules which separate the polymer chains and can be displaced by a chain segment more readily than can a segment of an adjoining chain. Boyer and Spencer¹⁰ in a study of the relationship between compatibility and plasticizer efficiency for polystyrene suggest that the

* Reprinted from the *Transactions of the Institute of the Rubber Industry*, Vol. 30, No. 5, pages 115-128, October 1954.

efficiency goes through a maximum as a function of the interaction parameter of the plasticizer and the polymer (μ).

Several approaches have been proposed to the mechanism of plasticizer action. Zhurkov¹¹ maintains that each plasticizer molecule blocks off an attractive site along the chain, thus preventing it from reacting with an adjacent molecule. Boyer and Spencer² suggest that a plasticizer might act by lowering the melt viscosity of the system. Fox and Flory⁴ found that t_g is related to the number average molecular weight of the polymer and suggest that the addition of a plasticizer simply lowers the average molecular weight. Boyer¹² points out that all of the approaches lead to the conclusion that the lowering of the second-order transition temperature is linear with regard to the weight or mole per cent of plasticizer.

Considerable work has been done in studying the efficiency of plasticizer action in various systems¹³. It is determined as the extent to which the property being studied is altered by a fixed amount of plasticizer. Since high molecular-weight copolymers of butadiene and styrene extended with large amounts of oily plasticizers have recently come into wide use, it was desirable to investigate the low-temperature characteristics of such mixtures and the possible influence of other plasticizers on the low temperature behavior of the copolymers. The work reported here is chiefly concerned with the maximum practical lowering of the transition temperature that can be achieved by a plasticizer in a butadiene-styrene copolymer and its relationship to the polymer-plasticizer interaction characteristics.

APPARATUS AND EXPERIMENTAL PROCEDURE

One of the simpler means of determining the glassy transition temperature of a polymer was used, namely, a study of the volume-temperature characteristics. In this method, the transition temperature is indicated by an abrupt change in the slope of the specific volume vs. temperature plot.

The experimental measurements were carried out in modified glass dilatometers of the type described by Bekkedahl and Wood¹⁴, using a silicone oil as the confining liquid. The bulb was made from 15 mm. O.D. Pyrex tubing and was about 5 inches long. It contained from 7 to 8 grams of polymer, cut into cubes of about 1 mm. It was sealed at the upper end to the measuring tube, which was precision-bore tubing (2.06 mm. i.d.) about 15 inches long. A snug fitting Pyrex plug inserted below the polymer enabled sealing of the bulb without degradation of the polymer and without increasing the net volume of the bulb. After evacuation, silicone oil (GESF81-40) was allowed to enter the dilatometer through a ground glass joint at the top of the measuring capillary. The silicone oil had no swelling effect on the polymer, and was found to have a linear volume-temperature dependence over the range of temperatures used. A paper scale graduated in mm. was fixed to the capillary and permitted the meniscus level in the capillary to be estimated to ± 0.1 mm. No stem corrections were applied for the exposed capillary, since interest was primarily in the transition temperature and not in absolute coefficients of expansion. Omission of the correction was found to affect only the slopes of the volume-temperature lines and not the value of t_g or the magnitude of the change of slope at t_g .

The bulb of the dilatometer was immersed in stirred ethanol in a four-quart Dewar flask, the temperature of the ethanol being adjusted to the desired level by the addition of dry ice for temperatures down to about -60°C , and by the addition of liquid nitrogen for temperatures from -60° to -105°C . At the

lowest temperatures, liquid nitrogen had to be added at frequent intervals (about two minutes) to maintain a constant temperature. No measurements were carried out at temperatures below -105°C in the work reported here. The temperature was measured with a platinum-resistance thermometer, enabling small changes and drifts of temperature to be detected instantly.

After reading the meniscus level at a given temperature, the bath was cooled by about 5°C and the meniscus again read after an interval of 15 minutes. It was found that thermal equilibrium was attained in about 10 minutes. A time dependence of t_g was found for only the most highly loaded blends. This resulted in a curved line at temperatures below about -92°C when readings were taken 15 minutes after temperature adjustments. The curvature disappeared, however, when the time interval was increased to 45 minutes. Further increases of the time interval by an additional 60 minutes did not alter significantly the slope of the line or the position of the break.

In order to determine the glassy transition temperature, it is not necessary to plot the specific volume of the polymer against the temperature. A simple plot of the level of the meniscus in the capillary against the temperature gives two straight lines intersecting at the transition temperature. Absolute values of the coefficient of expansion, β , were not calculated, but the change in the coefficient at the transition point was readily determined by the difference in the slopes of the two straight lines using the equation:

$$\Delta\beta = \frac{(s_1 - s_2) \times A}{v}$$

where s_1 and s_2 are the slopes of the lines above and below t_g , respectively, in $\text{cm./}^{\circ}\text{C}$.

A is the cross-sectional area of the capillary in cm.^2

v is the volume of polymer in cc. (assuming a polymer density of 0.91 g./cc.).

EXPERIMENTAL RESULTS AND DISCUSSION

The transition temperature and $\Delta\beta$ were determined for several types of polymers. The data are shown in Table I.

TABLE I
TRANSITION TEMPERATURE FOR DIFFERENT POLYMERS

No.	Polymer	t_g ($^{\circ}\text{C}$)	$\Delta\beta$ (cc./ml.)
1	50°C emulsion-polymerized 71/29 butadiene-styrene	-61.0	0.00032
2	5°C emulsion-polymerized 71/29 butadiene-styrene	-57.4	0.00033
3	5°C emulsion-polymerized 71/29 butadiene-styrene polymerized to high molecular weight	-58.0	0.00028
4	(3) blended with 30 per cent of a petroleum oil	-53.2	0.00027*
5	5°C emulsion polymerized 90/10 butadiene-styrene	-76.8	0.00028
6	50°C emulsion-polymerized butadiene	-84.5	0.00041
7	55°C emulsion-polymerized butadiene	-85.7	0.00043
8	sodium-polymerized polybutadiene	-51.8	0.00029
9	5°C emulsion-polymerized 64/36 butadiene-acrylonitrile	-32.8	0.00022
10	30°C emulsion-polymerized 64/36 butadiene-acrylonitrile	-29.5	0.00025

* Calculation based on polymer only.

In most cases the values are the averages of at least two determinations. The precision of t_g is $\pm 1^\circ \text{C}$, and was found to be independent of whether observations were made during heating or cooling in polymers that did not crystallize. The data show that temperature of polymerization and molecular weight have no appreciable effect on the transition temperature of the polymers studied. They also show the effect of bulky styrene molecules and of the highly polar acrylonitrile groups when copolymerized with butadiene. Measurements were also carried out on polybutadiene polymerized at lower temperatures, but it was

TABLE 2
REPRODUCIBILITY OF t_g DETERMINATIONS

Sample No.	t_g ($^\circ \text{C}$)	$\Delta\beta$ (cc./ml.)
1 (unextracted)	-60.5	0.00028
2 (unextracted)	-60.6	0.00030
3 (unextracted)	-60.2	0.00027
4 (extracted)*	-58.0	—
5 (extracted)*	-60.2	0.00027
6 (extracted)*	-59.0	0.00027

* The nonpolymeric material was extracted by refluxing for two one-hour periods with ethanol-toluene azeotrope, followed by drying under vacuum to constant weight.

found that some crystallization occurred in these polymers and raised the transition temperature. Subsequent studies were, therefore, restricted to non-crystallizing polymers.

The reproducibility of the determinations is shown in Table 2, where tests are reported on a number of samples of the high molecular-weight butadiene-styrene copolymer. The results show that the precision is about $\pm 1^\circ \text{C}$ for t_g and ± 0.00002 for $\Delta\beta$ and that the impurities in unextracted polymer have no effect on the values.

TABLE 3
TRANSITION CHARACTERISTICS OF POLYMER BLENDS

Polymers blended	Ratio (Parts by weight)	t_g ($^\circ \text{C}$)	$\Delta\beta$ (cc./ml.)
71/29 butadiene-styrene and polybutadiene	75:25	-61.5	0.00009
	50:50	-66.0	0.00007
	25:75	-70.5	—
	0:100	-84.5	0.00013
90/10 butadiene-styrene and 64/36 butadiene-acrylonitrile	50:50	-25 and -75	0.00011* and 0.0005
	35:65	-25	0.00017*

* If $\Delta\beta$ is calculated on the basis that only the butadiene-acrylonitrile polymer goes through a transition at this temperature, values of 0.00022 and 0.00026 respectively are obtained. These are similar to the values shown for the copolymer alone (see Table 1).

BLENDS OF POLYMERS

Two series of polymer blends were prepared on a rubber mill. The first was made up of the high molecular-weight butadiene-styrene (71/29) copolymer (No. 3 in Table 1) and polybutadiene, the second was a blend of a butadiene-styrene (90/10) copolymer and a butadiene-acrylonitrile (64/36) copolymer. The values of t_g and of $\Delta\beta$ are shown in Table 3.

The blends show two distinct types of behavior. Those of polybutadiene blended with butadiene-styrene copolymer show transition temperatures between those of the two pure components, the value varying with the composition, while those of the butadiene-styrene copolymer with the butadiene-acrylonitrile

copolymer show two separate transition temperatures, one characteristic of each component. In the first case the polymers appear to lose their individual transition characteristics and may be considered compatible, while in the second case they retain their individual transition characteristics and may be considered incompatible. In the case of the 35/65 blend of the latter polymers, the transition at -75°C was not detected, probably because insufficient butadiene-styrene copolymer was present to give a detectable break in the line.

ESTER PLASTICIZERS

A study was carried out on blends of the high molecular-weight butadiene-styrene (71/29) copolymer mentioned above (and referred to in the tables as XPRD-211) with each of eight ester plasticizers. In an effort to correlate the polymer-plasticizer interaction characteristics with the effect on t_g , the relative compatibilities of the plasticizers with the polymer were determined by measuring the swelling of a single gum stock of the polymer in each plasticizer.

TABLE 4
SWELLING OF GUM STOCK IN ESTER PLASTICIZER

Plasticizer	Supplier	Increase of length of 100 mm. strip (mm.)		F.P. ($^{\circ}\text{C}$)
		$+55^{\circ}\text{C}$ (158 hrs.)	-26°C (96 hrs.)	
Methyl phthalyl ethyl glycolate	Monsanto Chem. Co.	0.5	0.5	-40
Dicarbitol phthalate	Ohio Apex Inc.	1.5	1.5	-35
Tributoxyethyl phosphate	Ohio Apex Inc.	15.0	13.2	-70
Dibutyl phthalate	Carbide and Carbon Chem. Co.	31.3	28.5	-35
Diocetyl adipate	Ohio Apex Inc.	49.0	48.5	-91
Diocetyl sebacate	Resinous Products and Chemicals Co.	48.0	48.0	-55
Dibutyl sebacate	Resinous Products and Chemicals Co.	53.0	53.0	-20
Cardolite-7625	Irvington Varnish and Insulator Co.	43.5	—	-92

The method used was ASTM Committee D-11 Procedure D-471-49T Method B, in which a strip of compound 100 mm. in length and 1.6 mm. in width is died from a 3/32-in. thick tensile sheet and swollen in the liquid at $+55^{\circ}$ and -26°C until no further increase in length is observed. The results are shown in Table 4, together with the approximate freezing points of the plasticizer. No claim is made for the chemical purity of the plasticizers other than that of the suppliers.

It will be noted that the swelling effect ranged from an increase of length of the gum strip of 0.5 mm. for methyl phthalyl ethyl glycolate to an increase of 53.0 mm. for dibutyl sebacate. The swelling values at -26°C are only slightly lower than those at $+55^{\circ}\text{C}$, indicating that over this temperature range the plasticizers and polymer do not change appreciably with respect to compatibility.

Blends of polymer and plasticizer were prepared by banding the polymer on a cold mill and gradually adding the plasticizer, since this method permitted an accurate control of the amount of plasticizer in the blend. The mechanical breakdown of the polymer which occurred had no significant effect on the trans-

TABLE 5

 t_g AND $\Delta\beta$ OF MILL BLENDS OF POLYMER AND PLASTICIZER

Plasticizer	Weight per cent plasticizer	t_g (° C)	$\Delta\beta$ ($\times 10^4$)
Methyl phthalyl ethyl glycollate	9.3	-69.0	3.8
	11.2	-61.5	—
	20.8	-60.8	—
	28.3	-61.7	—
	28.6	-60.3	—
Dicarbitol phthalate	10.0	-60.5	3.2
	18.4	-60.3	3.8
	23.7	-62.2	3.7
	33.1	-61.5	3.9
	2.0	-62.5	3.1
Tributoxyethyl phosphate	9.5	-66.0	2.9
	17.6	-71.7	2.6
	24.4	-75.0	3.6
	33.6	-74.5	3.6
	33.3	-74.2	3.4
Dibutyl phthalate	9.4	-64.5	2.9
	16.8	-68.5	3.3
	24.0	-73.2	3.9
	30.1	-77.0	4.2
	37.9	-80.5	4.8
Diocetyl adipate	45.0	-81.7	6.0
	51.5	-82.8	5.7
	4.7	-63.2	—
	8.2	-64.7	3.2
	9.1	-65.0	2.9
Diocetyl sebacate	11.3	-68.3	3.4
	13.6	-74.0	3.7
	16.7	-73.8	3.5
	23.1	-77.7	4.3
	28.0	-79.5	3.7
Dibutyl sebacate	28.8	-80.9	4.0
	33.3	-84.5	—
	38.1	-87.8	6.6
	45.1	-87.5	5.7
	50.0	-94.0	5.4
Diocetyl sebacate	60.0	-95.0	—
	7.2	-63.2	3.2
	9.4	-65.2	2.9
	11.5	-67.3	3.0
	17.9	-73.8	3.4
Dibutyl sebacate	24.2	-80.7	3.9
	29.6	-82.0	4.7
	29.6	-80.6	3.6
	34.2	-86.0	5.3
	40.1	-85.0	4.2
Cardolite-7625	51.7	-93.0	—
	60.0	-96.0	—
	4.6	-65.0	3.0
	20.6	-68.8	2.8
	31.9	-68.1	2.9
Cardolite-7625	39.2	-68.2	3.5
	45.9	-67.0	3.2
	12.9	-68.2	3.5
	25.7	-79.5	4.5
	27.0	-81.8	4.7
Cardolite-7625	38.1	-82.8	5.9
	41.2	-87.0	5.8

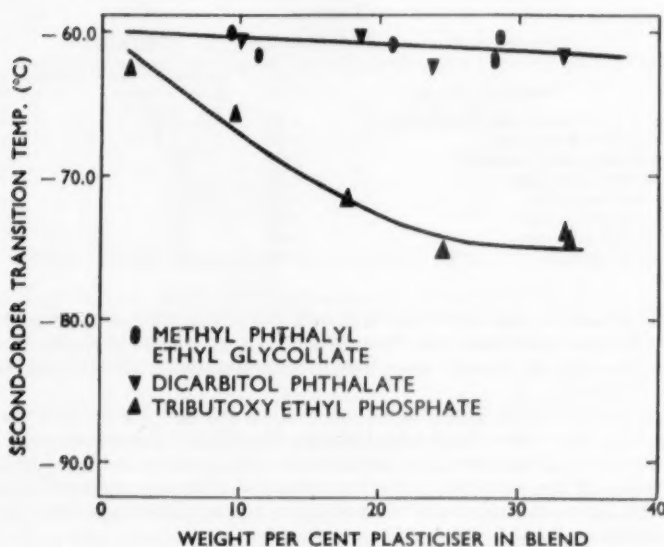


FIG. 1.—Effect of ester plasticizers on t_g of butadiene-styrene copolymers.

ition characteristics. For each blend, a volume-temperature study as described above was carried out. The values of t_g and of $\Delta\beta$ are shown in Table 5.

It is evident from a study of the data of Tables 4 and 5 that those plasticizers which do not swell the gum stock do not lower the t_g of the polymer in the blend. But those plasticizers which swell the polymer lower the transition temperature by an amount which correlates with the amount of plasticizer in the blend and with the compatibility as measured by swelling. The relationships are illus-

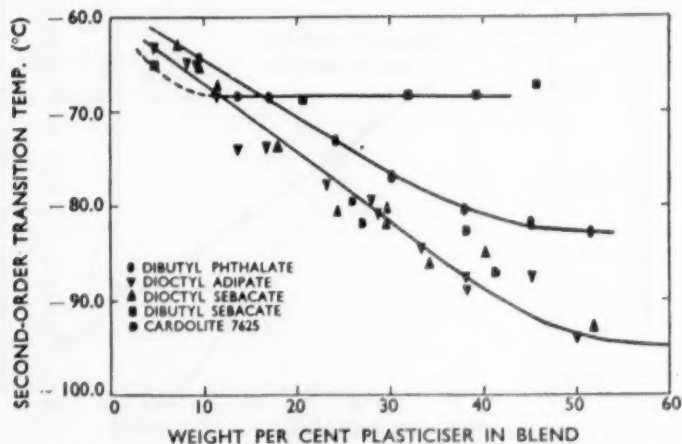


FIG. 2.—Effect of ester plasticizers on t_g of butadiene-styrene copolymers.

TABLE 6
EFFECT OF ESTER PLASTICIZERS ON t_g OF XPRD-211

Plasticizer	F.P. (° C)	Swelling increase at 55° C (mm.)	Minimum value of t_g (° C)
Methyl phthalyl ethyl glycolate	-40	1.0	-61
Dicarbitol phthalate	-35	1.5	-61
Tributoxyethyl phosphate	-70	15	-75
Dibutyl phthalate	-35	31	-83
Diocetyl adipate	-91	49	-95
Diocetyl sebacate	-55	48	-95
Dibutyl sebacate	-20	53	-68
Cardolite-7625	-92	43.5	about -90

trated in Figures 1 and 2, in which t_g of each blend is plotted against its composition. Blends containing more than 60 per cent by weight of plasticizer could not be prepared on the mill, since they became too sticky and adhered strongly to the mill rolls.

The data of Table 5 and the curves of Figures 1 and 2 show that the more compatible these ester plasticizers are with the polymer (as measured by swelling), the lower is the transition temperature which can be achieved in blends. The values of the maximum lowering estimated from the curves of Figures 1 and 2 are shown in Table 6 and plotted in Figure 3 against the increase in length on swelling at +55° C.

With the exception of that for dibutyl sebacate, the points fall on a fairly straight line, illustrating the direct relationship between the swelling of this butadiene-styrene copolymer by ester plasticizers and the efficiency of these plasticizers in lowering the transition temperature of the polymer. The point for Cardolite-7625 is drawn with dotted lines, because insufficient determinations were made at high loadings to establish the actual minimum value of t_g attainable.

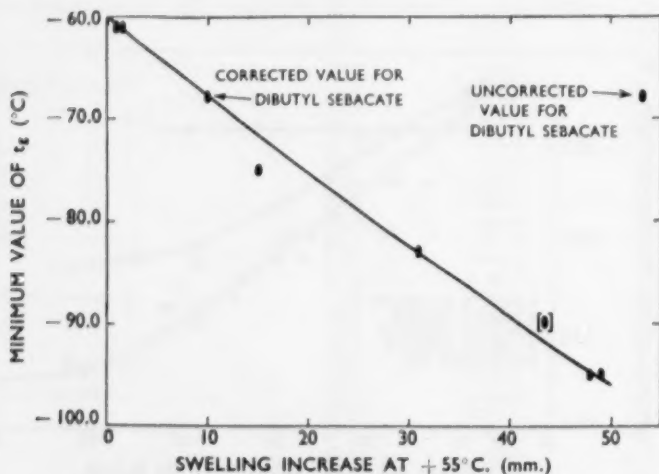


FIG. 3.—Minimum value of t_g of blends vs. swelling increase at +55° C.

TABLE 7
CRYSTALLIZATION OF BLENDS OF XPRD-211 AND DIBUTYL SEBACATE

Weight-per cent plasticizer	Δ Specific volume at -45°C (cc./ml.)
16.7	2.5
23.1	6.4
28.6	11.0
33.3	14.3

THE BEHAVIOR OF DIBUTYL SEBACATE

Swelling the gum stock in dibutyl sebacate increased its length by 53 mm., but the minimum t_g of blends is only -68°C . This value was obtained for blends containing appreciable amounts of plasticizer. In these blends, crystallization of the plasticizer, as shown by a marked decrease in specific volume, occurred over the range from about -20°C to about -45°C . The amount of crystallization was a function of the temperature and not appreciably time dependent as is the case for high polymers.

The amount of crystallization was calculated, as change of specific volume, from the difference between the meniscus level in the dilatometer for the crystallized polymer and for amorphous polymer at the same temperatures. The latter value was obtained by extrapolation of the linear volume-temperature line obtained at higher temperatures. The amount of crystallization was determined at -45°C for each of the dibutyl sebacate blends by cooling the

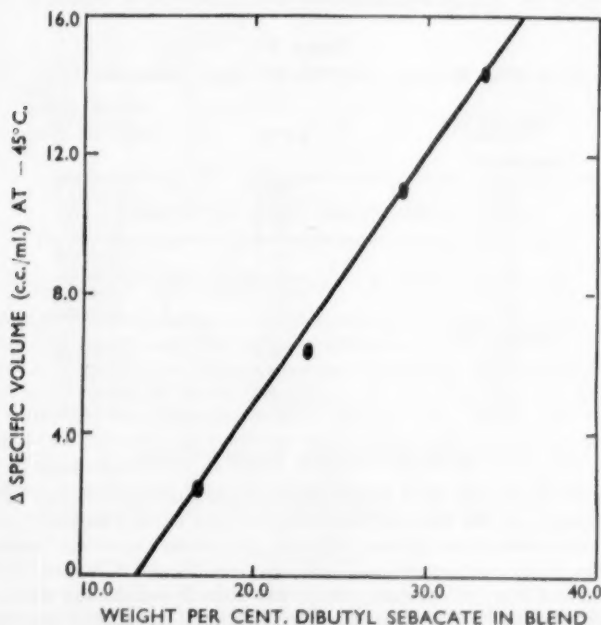


FIG. 4.—Crystallization in blends at -45°C vs. weight-per cent dibutyl sebacate.

dilatometers from 0° C in five degree intervals and maintaining a constant temperature until no further significant change of volume with time was noted. The data are presented in Table 7 and Figure 4.

The relationship between the composition of the blend and the amount of crystallization is a straight line which extrapolates to 13.2 per cent dibutyl sebacate for zero crystallization. Apparently for amounts of dibutyl sebacate greater than 13.2 per cent of the blend, the attraction between plasticizer molecules at temperatures below about -20° C is greater than the attraction be-

TABLE 8
SWELLING OF GUM STOCK IN PETROLEUM PLASTICIZERS

	Increase of length of 100 mm. strip	
	+55° C (in 168 hrs.)	-26° C (in 96 hrs.)
Sundex-53	45.5	47.0
Circosol-2XH	37.0	37.0

tween plasticizer and polymer. One might speculate that this amount of plasticizer remains bound by van der Waals forces to the polymer at low temperature, and that this may be enough plasticizer to form a monomolecular layer between adjacent polymer molecules, or that with this amount of plasticizer there are sufficient molecules to block all attractive sites along the chains.

When a correction is made in the swelling value for the fact that, below -45° C, only 13.2 per cent plasticizer remains as a swelling agent for the polymer, the value for dibutyl sebacate also falls on the line of Figure 3.

TABLE 9
 t_g OF MILL BLENDS OF XPRD-211 WITH PETROLEUM OILS

Weight-per cent plasticizer	t_g (° C)	Δ Coeff. of exp. (cc./ml.) on XPRD-211 portion
Sundex-53		
3.2	-58.4	0.00028
6.8	-59.7	0.00041
8.6	-55.2	0.00031
11.8	-55.0	0.00022
18.7	-55.7	0.00023
25.0	-54.4	0.00030
37.2	-55.0	0.00049
50.1	-57.7	0.00055
Circosol-2XH		
16.7	-58.0	0.00043
28.6	-58.0	0.00047
37.5	-59.3	0.00048
50.0	-57.4	0.00082

PETROLEUM OIL PLASTICIZERS

The most commonly used extenders for high molecular-weight butadiene-styrene copolymers are the petroleum oils. They behave entirely differently from the ester plasticizers in their effect on the glassy transition temperature. Two of the most commonly used oils, Sundex-53 and Circosol-2XH, both products of the Sun Oil Company, were tested in the same way as the esters. The increase of length of the swelling strips (Table 8) shows that they are highly compatible with the polymer.

Blends containing from 0 to 50 per cent oil were prepared on the mill and their transition temperatures determined. The results in Table 9, and Figure 5 show that, although the oils swell the gum stock appreciably, they do not lower the transition temperature but actually raise it slightly.

Further studies, with more highly purified oils, must be carried out to explain the action of the petroleum oils. Since they are highly compatible with the polymer and since the transition temperature is actually raised slightly, it appears that the action is similar to that with blends of polybutadiene and butadiene-styrene copolymers in which the transition temperature is between those of the two components. Sundex-53 and Circosol-2XH become stiff and nonflowing in the approximate ranges of -20° to -35° C and of -30° to -40° C, respectively, and undoubtedly both contain some relatively long chain molecules.

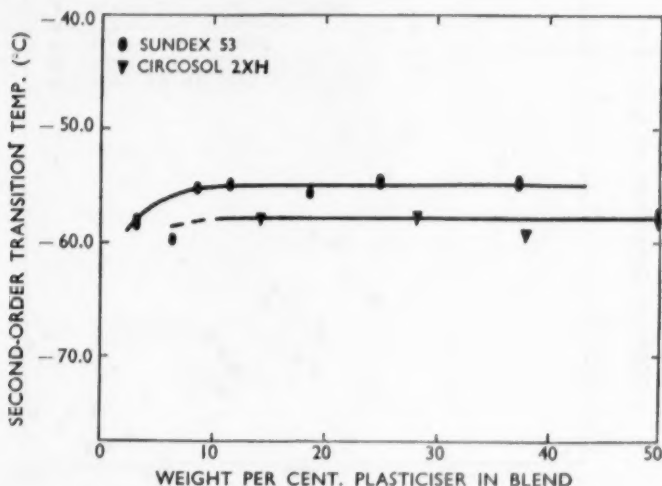


Fig. 5.—Effect of petroleum oils on t_g of butadiene-styrene copolymers.

CHANGE IN THE COEFFICIENT OF EXPANSION AT t_g

The change of the coefficient of expansion of the polymer at t_g has been calculated for most blends, and the values are included in the various tables. It was pointed out earlier that, for unplasticized polymers, the change of the coefficient is characteristic of the comonomers present. The value for each blend is plotted against its transition temperature in Figure 6. Since these values are characteristic of the polymer behavior at t_g , one might expect to be able to represent all the data by a single line. It appears from the data, however, that different lines exist for the different plasticizers. The data would seem to be affected by some property of the plasticizer as yet unspecified.

CONCLUSIONS

It has been found that the effect of ester plasticizers on the second-order transition temperature in blends with butadiene-styrene copolymers is related to plasticizer-polymer compatibility, determined by swelling of the polymer

gum stock in the plasticizer. Plasticizers with the greatest swelling effect on the polymer are found to be the most efficient in lowering the transition temperature, and are capable of lowering it to a greater degree. Of the eight ester plasticizers tested, one, dibutyl sebacate, partially crystallized at low temperatures. However, enough of it remained intimately associated with the polymer to cause a lowering of the transition temperature from -60° to -68° C. It would be desirable to make the swelling measurements in the region of t_g . Since this is impractical, work is now in progress to determine the effect of physical state of the plasticizer at the transition temperature.

The petroleum oil plasticizers were highly compatible with the polymer. However, instead of producing blends with lowered values of t_g , they produced

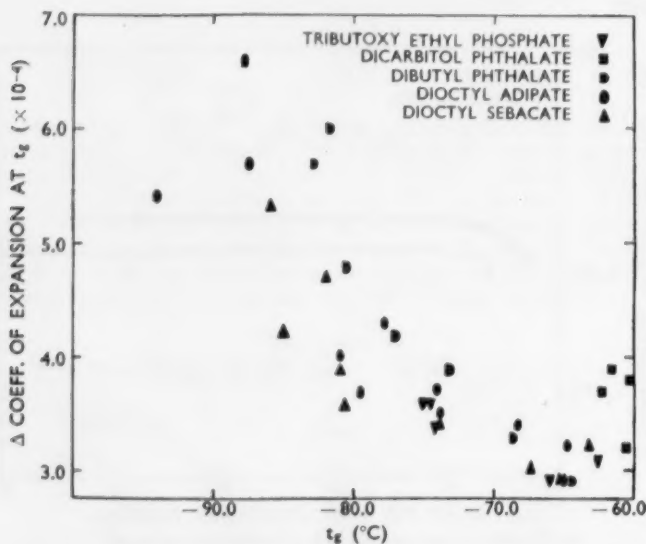


FIG. 6.— $\Delta\delta$ vs. second-order transition temperature.

blends with slightly higher values of t_g . Further work has been initiated to explain this phenomenon.

SUMMARY

The second-order transition temperatures of plasticized butadiene-styrene copolymers have been measured by dilatometric techniques. In a series of ester plasticizers, the ability of a given plasticizer to depress the second-order transition temperature of the polymer is related to the swelling effect of the plasticizer on the polymer. The special case of a crystallizing plasticizer (dibutyl sebacate) has been discussed. Common petroleum plasticizers do not appear to behave in a similar manner. The change of coefficient of expansion of the ester-plasticized copolymers is related to the measured transition temperature of the blend.

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VULCANIZING VARIABILITY OF NATURAL RUBBER IN PURE-GUM AND CARBON BLACK COMPOUNDS *

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INTRODUCTION—THE ACS 1 COMPOUND

For many years the routine evaluation of the vulcanizing properties of rubber was determined by its behavior in a rubber-sulfur compound without other added ingredients, and most of the voluminous literature on variability prior to 1930 is based on the results of these tests. When organic accelerators first became popular, one of the advantages claimed for them was that they eliminated variability. At that time it was customary to use what today would be regarded as excessive amounts of vulcanizing ingredients, and under these conditions work at the London Advisory Committee laboratories confirmed that the excessive variability of the rubber-sulfur compound largely disappeared. With the advent of modern compounds, however, containing minimum amounts of sulfur and accelerator, variability in vulcanization again became an important manufacturing problem, which the London Advisory Committee attributed to the fact that the minimum dosage of vulcanizing ingredients for satisfactory results is not the same for all rubbers.

At that time, many different accelerators were in commercial use, only a few of which have retained their popularity. The relative vulcanizing behavior of different rubbers depended on the accelerator, and producers had little to guide them in selecting the most suitable formula for a test compound. During the early 1930s, the London Advisory Committee, in consultation with British manufacturers, developed a pure-gum test compound containing mercaptobenzothiazole as accelerator, which was eventually approved with slight modification by the American Chemical Society¹. This modified compound is now known as ACS 1 and is used for routine test purposes throughout the rubber growing industry. Its composition by weight is as follows: rubber 100, zinc oxide 6, sulfur 3.5, stearic acid 0.5, mercaptobenzothiazole 0.5.

This compound is now being used for the technical classification of rubber, and it is the purpose of this paper to consider how the results agree with those given by other pure-gum compounds and, in particular, with the behavior of rubber in the more complex compounds essential to successful manufacture.

Data are given in Table 1 for the variability in the ACS 1 compound of single sheets of estate rubber, shown by six surveys in Ceylon and Malaya. Included is one carried out in 1944 by Rubber Research Institute of Malaya according to plans prepared before the Japanese invasion. It is unfortunate that the most comprehensive survey yet envisaged should have been carried out under such adverse conditions, but the results have been included because the internal evidence suggests that testing was reasonably carefully carried out, and

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 30, No. 6, pages 162-180, December 1954.

TABLE I
VARIABILITY OF NATURAL RUBBER IN THE ACS 1 COMPOUND. MODULUS AT A FIXED CURE

Literature reference	Authors	Date	Country	Scope of survey	Type of rubber	Vulcanizing		Modulus at elongation (%)	Range (kg./cm. ²)	Mean (kg./cm. ²)	s.d. (kg./cm. ²)	c.v. (%)
						Temp. (°C)	Time (min.)					
2	Hastings and Rhodes	1939	Malaya	157 estates	RSS 1	127	60	700* (i.e.)	—	52	12.3	23.7
4	Philpott	1940	Ceylon	72 estates	Crepe and sheet	127	60	700* (i.e.)	26-82	45.3	10.2	22.5
5	R.R.I. Malaya	1944	Malaya	262 estates	Sheet	127	60	700* (i.e.)	—	62	16.5	26.6
6	Newton et al.	1949	Malaya	48 estates	RSS 1	140	40	600 (i.e.)	18-66	33	7	21.2
7	R.R.I. Ceylon and L.A.C.	1950-51	Ceylon	29 estates	RSS 1	140	40	660 (i.e.)	38-86	63.2	12.3	19.5
8	Bocquet	1946	Indo-China	10 estates over 5 years	Sheet	127	40	600 (i.e.)	8-69.5	31.4	6.0	19.0
9	A.C.S. Crude Rubber Committee	1940	U.S.A.	16,981 tests on factory blended batches by one manufacturer	RSS 1	126	40	700	60-155	99	12.6	12.7

* i.e. = internal circumference.

† s.d. = standard deviation; c.v. = coefficient of variation.

because they fit well into the general picture. It is noteworthy that the range covered by the coefficients of variation is fairly narrow, 19 to 26.6 per cent, and that the ranking of the six surveys in order of coefficient of variation is identical with that by the number of estates participating in each survey.

This latter observation is consistent with the data of the 1944 survey, which provided strong evidence of a regional effect due to geographical factors, such as different soil types and lie of land.

It is also evident from Table 1 that variation in Ceylon is similar to that in Malaya, and this similarity is probably genuine, since it is known that the testing methods in use in the two countries in 1939 gave results in excellent agreement.

Table 1 also includes published figures for a very large number of blended batches of RSS 1 passing through a single American factory prior to 1940. The U. S. manufacturer's data are less variable, but this may be due to the use of bale samples, each consisting of many sheets, instead of single sheets as in the Far Eastern surveys. The use of blended batches would itself reduce the variability in inverse relation to the square root of the number of batches being blended.

According to Hastings and Rhodes², the pattern of variability in the ACS 1 compound is similar to that in the rubber-sulfur (RS) compound, and a recent statistical analysis has indicated a correlation coefficient of about 0.7 for not very widely differing modulus results from 9 clones growing in 36 plots at the Rubber Research Institute of Malaya Experiment Station³.

Dinsmore in 1926 gave results of tests on a number of rubbers, each vulcanized with a range of accelerators and also in a RS compound¹⁰. When the accelerator results for each rubber are averaged, they show almost perfect correlation with the results given by the RS compound. Some of these accelerators are no longer used and the correlation is misleading, for recent experiments have shown that, although RS modulus is well correlated with modulus in M.B.T. and M.B.T.-T.M.T. compounds, in a D.P.G. compound the correlation is only fair. Indeed, complete reversal of behavior can occur, i.e., a rubber giving the highest modulus in the M.B.T. compound may give the lowest in the D.P.G. compound¹¹. Mercaptobenzothiazole and chemically similar accelerators tend, however, to show the same differences between rubbers, and since this class of accelerator is most widely used, these differences are of greatest importance.

EFFECT OF CARBON BLACK ON VARIABILITY

None of the test compounds which have been used for natural rubber is of value for testing general-purpose synthetic rubber, which requires the addition of an appreciable amount of carbon black in order to obtain reasonable mechanical properties.

When natural rubber is compounded with carbon black, some of its effects are comparable to a type of vulcanization, and it cannot be taken for granted that the relative vulcanizing behavior of natural rubbers is the same, irrespective of the presence of active loading material.

A study of the variability of natural rubber in carbon black compounds was commenced shortly before the War and was eventually resumed as opportunity offered in London and Malaya. A complicating factor is the variety of types of carbon black used in industry and the arrival on the market of new and improved types which may profoundly modify conclusions drawn from the work so far completed. Another difficulty is that the results of tests in carbon black

compounds are not usually so reproducible as the results of tests in pure-gum compounds.

The most convenient and popular method of assessing the state of vulcanization is still the measurement of modulus after fixed periods of vulcanization at a single temperature. For pure-gum compounds the method can be related to the formation of cross-links¹², but for loaded compounds the issues are more complicated. Nevertheless modulus measurements are used for control purposes in industry and would, therefore, appear to be suitable for studying the comparative behaviors of different rubbers in the presence of carbon black.

The results shown in Table 2 were obtained at intervals on miscellaneous sets of samples, tested in the ACS 1 compound and in M.B.T. tread compounds containing 50 parts p.h.r. of MPC black¹⁴. By comparing the coefficients of

TABLE 2
COMPARISON BETWEEN MODULUS IN ACS 1 AND MPC TREAD
COMPOUNDS CONTAINING 50 PARTS BLACK P.H.R.

Source of rubbers	No. of samples	Coefficient of variation (%)		MPC modulus (kg./cm. ²) range	Correlation coefficient ACS 1 vs. MPC modulus
		ACS 1	MPC		
Miscellaneous specialty and commercial sheets	8	*43.4	10.0	39	0.83 (ss)
Miscellaneous samples from Malayan survey ³ , 1949	11	*41.0	8.1	29	0.86 (sss)
		†41.0	8.4	22	0.70 (s)
Sheet samples from 20 clones growing in Field 15, R.R.I. (Malaya) Experiment Station	20	†23.0	7.9	24	0.75 (sss)
Clonal and smallholders' sheets, R.R.I.E.S. (Malaya)	10	†27.0	5.3	12	0.77 (ss)
Clonal sheets mostly of "500 series" R.R.I.M.E.S.†	16	†31.2	6.0	25	0.66 (ss)

* Tested in U.K.

† Tested in Malaya.

‡ Unpublished data of H. M. Edmondson.

Coefficient of variation for mixing, curing and testing approximately 4 per cent, for both ACS 1 and MPC compounds.

Levels of significance for correlation coefficient: s = 5 per cent; ss = 1 per cent; sss = 0.5 per cent.

variation given in the table, it is obvious that carbon black has reduced considerably the differences between the moduli of different rubbers. Moreover, the variation in the ACS 1 compound is mostly due to genuine differences in the vulcanizing behavior of the samples, whereas an appreciable proportion of the small differences in the carbon black compound can be ascribed to the overall errors of mixing, curing and testing, which usually correspond to a coefficient of variation around 4 per cent for both pure-gum and tread compounds. The correlation between the results in the two compounds, although statistically significant, is imperfect, and frequent anomalies may therefore be expected. It is of interest to compare the variability of natural rubber in respect to modulus at a fixed cure in a black compound, since this type of test is extensively used to control the uniformity of synthetic rubbers.

Column 4 of the table gives the range in kg. per sq. cm. for each of the groups examined, the first two of which contain selected samples representing the extremes of naturally occurring variability. It is probably fair to set this at

about 30 kg. per sq. cm. in the type of compound employed if only RMA grades are considered. This figure may, therefore, be compared with the permissible tolerance allowed for GR-S.

For a 50 minute cure at 292° F, the specified modulus for GR-S is from 850 to 1200 lb. per sq. in. and for 100 minutes 1300 to 1700 lb. per sq. in., equivalent to ranges of 24.6 and 28.1 kg. per sq. cm., respectively¹². The variability exhibited by natural rubber in tread compounds in regard to modulus is, therefore, of the same order as that which American manufacturers are willing to accept as denoting uniform GR-S, and it may consequently be inferred that, if natural rubber were tested in the same way as GR-S, it would be regarded as substantially uniform. Certainly within any one technical class, natural rubber-carbon black vulcanizates are considerably more uniform in modulus than is required by the GR-S specification.

TABLE 3
MODULUS IN TIRE-TREAD SKELETON PURE-GUM COMPOUNDS
MPC compound:—Rubber 100, zinc oxide 5, stearic acid 2, sulfur 3, m.b.t. 1
HAF compound:—Rubber 100, zinc oxide 5, stearic acid 2, sulfur 2.5, Santocure
RF 1 0.8

Accelerator	Black	Modulus classification of rubber	600% Modulus at 30 min. cure (kg./cm. ²)	600% Optimum modulus (kg./cm. ²)	Optimum cure at 141° C (min.)
M.B.T.	Nil	High	78	82	20
		Medium	70	70	20-30
		Low	56	59	40
	5 p.h.r. MPC	High	86	86	30
		Medium	86	87	40
		Low	72	85	60
Santocure RF1	Nil	High	94	94	30
		Medium	91	91	30
		Low	76	83	40
	5 p.h.r. HAF	High	136	136	30
		Medium	137	137	30
		Low	126	127	30-40

This conclusion is strengthened by the results, given in Table 3, of experiments in which the addition of as little as 5 parts p.h.r. of either MPC or HAF black is sufficient to decrease appreciably modulus differences between rubbers at a fixed cure and almost eliminate differences in optimum modulus in the presence of MPC black. Rate of cure differences based on the time required to reach optimum modulus are, however, still present.

The same three rubbers were also vulcanized at a fixed cure near the optimum modulus in six inner-tube compounds. The main results are shown in Table 4. There is usually little difference in the modulus values yielded by the three rubbers, whether the chief loading ingredient is P.33 black or a mixture of activated whiting and red tube reclaim. Only when the chief loading material is activated whiting without reclaim do the low and high modulus rubbers exhibit appreciable differences in modulus. It is known that there is good correlation between results in the ACS 1 and in M.B.T./T.M.T. compounds¹¹, so any differences from the ACS 1 classification may be ascribed to the fillers in question.

From these experiments it is concluded that rubbers which exhibit important modulus differences in the ACS 1 compound tend to lose these differences in the

presence of loading materials, particularly carbon black. When rubbers have exceptionally high or low modulus figures in the ACS 1 compound, appreciable differences in modulus are still found in a black compound (e.g., the 39 kg. per sq. cm. range for the first group of rubbers in Table 2). It is clear, therefore, that the measurement of modulus in loaded compounds is not a sensitive index of variation, and that differences experienced by manufacturers in the behavior of high, medium, and low modulus rubbers are not likely to be associated with important differences in the modulus of the freshly vulcanized article. Only results for rubbers outside the classification range are likely to exhibit appreciable abnormalities of modulus.

In regard to properties other than modulus, a limited amount of information has been gained in Malaya and London on the behavior of commercial rubbers differing widely in ACS 1 modulus, when compounded in tire-tread type compounds.

TABLE 4
INNER-TUBE COMPOUNDS

ACS 1 Classification of rubber	Modulus at 500% elongation at a fixed cure near the optimum (kg./cm. ²)					
	A	B	C	D	E	F
High modulus	104	80	71	93	66	62
Medium modulus	104	80	68	96	63	61
Low modulus	106	80	66	81	65	60
	Principal ingredients					
	A	B	C	D	E	F
Rubber	100	100	100	100	58	45
Red tube reclaim	—	—	—	—	46	90
P.33 black	40	40	—	—	—	—
Activated whiting	—	—	30	30	20	60
Accelerator(s)	M.B.T.	M.B.T.	M.B.T.	M.B.T.	M.B.T.S.	M.B.T.S.
	M.B.T.S.	T.M.T.	T.M.T.	T.M.T.	Z.D.C.	Z.D.C.
	Z.D.C.			Z.D.C.		

Although modulus differences were small, sometimes appreciable differences were observed for optimum tear strength and resilience and Mooney scorch rate. Recently results have been published for the scorch rate and stress-strain properties of Red, Yellow, and Blue technically classified rubbers compounded in HAF treads containing three different accelerators¹⁴. In all cases, the Red rubber was the least and the Blue rubber the most scorchy. Elongation at break was independent of the technical classification grade, while modulus and tensile differences were either negligible, or did not exceed about 10 per cent.

DETAILED STUDY OF PROPERTIES IN TECHNICAL COMPOUNDS

It was felt that more detailed information regarding the behavior of technically classified rubber in carbon black compounds was required, and to this end a comparative study has been carried out on single bales of Red, Yellow, and Blue grades of RSS 1, in the ACS 1 compound, carbon black tread, and sidewall compounds.

The tread compounds contained either MPC or HAF black. For each type of black, one compound with conventional acceleration was used, and another accelerated with diphenylguanidine. Although rarely used in tread

compounds, diphenylguanidine was chosen as representing a class of accelerator chemically unlike mercaptobenzothiazole and its derivatives.

Details of the compounds used and of the experimental procedure are given in the Appendix.

The strain values at 5 kg. per sq. cm., on which the three bales were classified, viz., Red 96, Yellow 79.5, Blue 64.5, were approximately in the center of the respective grades, as redefined January 1, 1954. The range between the Red and Blue rubbers is, therefore, about two-thirds of the total permitted range of strain values for technically classified rubber.

Physical tests of the vulcanizates from the different compounds were carried out both before and after a short period of oven aging, viz., 4 days at 70° C. If oven-aging tests at 70° C. can be regarded as giving useful information about the natural life of vulcanizates, the results should give a comparative indication of the behavior of Red, Yellow, and Blue rubbers when still giving useful service.

The results of Mooney scorch tests are given in Table 5 and of physical tests in Tables 6 to 14.

TABLE 5
MOONEY SCORCH PROPERTIES OF RED, YELLOW, AND BLUE RSS 1 BALES

Compound	Accelerator	No. of mixes for each color grade	Average Mooney scorch time to reach (minimum + 5) (mins.)			Average Mooney rate of cure (25/T25) units/min.		
			Red	Yellow	Blue	Red	Yellow	Blue
ACS 1	MBT	2	20.5	11.5	9.6	4.95	5.90	9.15
MPC Tread	MBT	5	26.4	24.2	21.7	3.52	3.62	4.33
HAF Tread	Santocure	2	27.9	22.2	24.7	2.09	3.03	3.10
SRF Sidewall	RF1	2	37.2	26.9	29.9	2.72	3.84	4.04
	Santocure							
MPC Tread	DPG	2	>60	>60	51.0	—	—	—
HAF Tread	DPG	3	31.0	29.3	26.3	0.74	0.83	0.85

Standard deviations of single results:—Scorch time, 1.7; rate of cure, 0.5.

It is impracticable to present in detail the mass of data accumulated in these experiments, whether as tables or as charts. A selection has therefore been made of optimum values for each property (Tables 6 to 12), and the property/time of vulcanization curves examined to provide comparisons of (1) the time required to reach a fixed proportion (varied for each property) of the optimum value, and (2) the time required to reach a fixed value (Tables 13 and 14). Of these criteria, (1) is a measure of the rate of cure, and (2) is of obvious practical importance, as for example, when a specified level of a given property has to be reached.

MOONEY SCORCH PROPERTIES

The results given in Table 5 are the average of single tests for the number of mixes indicated in column 3 of the table. The method of determining the Mooney cure rate given in the Appendix is essentially similar to that described by Shearer, Juve, and Musch¹⁴.

In all compounds, Blue rubber scorches more quickly than Red, and in critical processing conditions, the differences could be of practical importance. Yellow rubber, however, behaves anomalously in the Santocure compounds, but subsequent scorching, as indicated by the Mooney cure rate, ranges the rubbers in every case in the order predicted by the technical classification.

TABLE 6
TENSILE STRENGTH

Compound	Aging	Kg. per sq. cm. at optimum		
		Red	Yellow	Blue
ASC 1 pure-gum	Before	101	115	138
	After	134	151	183
MPC/MBT tread	Before	198	204	216
	After	198	199	211
HAF/RF1 tread	Before	185	189	202
	After	172	181	194
SRF/RF1 sidewall	Before	198	214	227
	After	225	232	243
MPC/DPG tread	Before	197	192	203
	After	123	116	137
HAF/DPG tread	Before	188	188	183
	After	135	130	133

Previous tests have shown that the correlation between scorch times and moduli in the ACS 1 compound is of a high order, viz., 0.82 for scorch time vs. strain, and -0.82 for scorch time vs. 600 per cent modulus, both for 123 pairs of results⁶.

The present results show that the use of a modulus measurement in the ACS 1 compound as a means of technical classification is of practical value in determining the scorch rate in a carbon black compound.

OPTIMUM TENSILE STRENGTH

It is clear from Table 6 that, apart from the DPG compounds, Blue rubber has a higher tensile strength than Yellow, and Yellow than Red, and that carbon black only affects the extent of the difference. The differences of tensile strength are maintained after aging. The order of superiority of Blue over Red is 35 per cent in the ACS 1 and 10 per cent in the black compounds.

OPTIMUM MODULUS

In the ACS 1 compound there are marked differences in the optimum modulus (Table 7). These differences correspond to the original classification which is based on modulus or strain values after a fixed period of cure.

TABLE 7
300% MODULUS

Compound	Aging	Kg. per sq. cm. at optimum		
		Red	Yellow	Blue
ACS 1 pure-gum	*Before	44	52	66
	*After	84	108	132
MPC/MBT tread	Before	115	116	118
	After	137	136	142
HAF/RF1 tread	Before	136	140	144
	†After	103	104	106
SRF/RF1 sidewall	Before	49	56	57
	After	74	80	83
MPC/DPG tread	Before	128	130	130
	After	119	106	126
HAF/DPG tread	Before	157	155	149
	After	128	136	133

* 600% modulus.

† 200% modulus.

Similar differences occur between the rubbers after aging, when optimum modulus values are much higher.

On loading with carbon black, the differences in moduli remain in the decreasing order: Blue, Yellow, Red, and are small for the tread compounds. As would be expected because of the lower loading of black, the sidewall compound shows larger percentage differences.

Aging affects the value for optimum modulus but not the differences between rubbers.

In the DPG/black compounds, the differences between the three rubbers are small and not consistently in accord with the original classification. However, the use of DPG alone is infrequent and such anomalies will be rarely met.

There is evidence from other properties that the original differences in curing properties of the three rubbers are maintained even in the presence of carbon black, and this is also true of modulus at cures shorter than the optimum. The present results provide further confirmation of the claim made earlier in this paper that it would have to be a very exceptional natural rubber which fails to fall within the wide range of modulus permitted for synthetic rubber. Whereas

TABLE 8

HARDNESS

Compound	Aging	Degrees B.S. at optimum		
		Red	Yellow	Blue
ACS 1 pure-gum	Before	36.5	37.7	39.7
	After	39.3	41.4	43.3
MPC/MBT tread	Before	72.9	73.9	73.0
	After	75.8	75.9	76.4
HAF/RF1 tread	Before	64.3	64.4	66.1
	After	69.1	68.6	69.6
SRF/RF1 sidewall	Before	51.6	53.6	53.9
	After	53.8	54.8	56.0
MPC/DPG tread	Before	71.5	71.8	70.2
	After	71.2	71.4	69.5
HAF/DPG tread	Before	66.9	66.5	66.3
	After	66.9	67.8	66.5

the ACS 1 mix might be said to exaggerate the differences between natural rubbers, it can equally be argued that the tests used for synthetic rubber hide the differences.

OPTIMUM HARDNESS

Hardness degrees B.S. correspond to modulus at low strain expressed in logarithmic units. It is not surprising, therefore, that the hardness values in Table 8 tend to fall in line with modulus values.

The differences between the rubbers are mostly small in the presence of black, and the results of tests on black compounds are not as reproducible as those on pure-gum compounds, due to local variations in test specimens. Nevertheless, the MBT and with Santocure RF1 acceleration, Blue rubber is consistently harder than the others, except for one anomalous result, when the Yellow rubber is a little harder. Similarly Red rubber, with one exception, is softer than the other two. As with modulus, the differences are most marked in the sidewall SRF compound, where they are rather more than half those in the ACS 1 compound.

In the two DPG compounds, Blue rubber is appreciably softer than either Red or Yellow, which are about equal.

TABLE 9
RESILIENCE

Compound	Aging	Per cent at optimum		
		Red	Yellow	Blue
ACS 1 pure-gum	Before	79.0	81.1	85.1
	After	86.8	85.8	89.2
MPC/MBT tread	Before	60.8	61.3	63.7
	After	61.3	61.8	63.5
HAF/RF1 tread	Before	68.0	68.5	69.4
	After	69.0	70.1	69.9
SRF/RF1 sidewall	Before	83.8	84.7	86.4
	After	86.0	86.1	87.1
MPC/DPG tread	Before	62.2	60.9	64.3
	After	62.2	62.1	65.2
HAF/DPG tread	Before	68.5	67.2	69.5
	After	67.4	67.9	68.7

The differences between rubbers are unaffected by aging, which generally causes an increase of the hardness.

OPTIMUM RESILIENCE

An outstanding feature of the results of resilience tests (Table 9) is the consistently high values in all but one case (aged HAF/Santocure RF1 tread) given by Blue rubber. Yellow rubber is also superior to Red, though to a less marked degree, except in DPG black compounds. In contrast to hardness, the differences are more marked in MPC than in HAF compounds, are not outstanding in the SRF compound, and in the DPG compounds the technical classification order is maintained. The overall picture is little affected by aging.

OPTIMUM TEAR STRENGTH

In all compounds, Blue rubber has the highest tear strength, before and after aging, and in some cases the difference is outstanding, e.g., MPC/MBT tread (Table 10). Yellow rubber generally has a higher tear strength than Red.

OPTIMUM CRACK GROWTH

The results of de Mattia crack growth tests given in Table 11 show that, once a steady state is reached (3-7 mm.), Red rubber gives the lowest rate of

TABLE 10
TEAR STRENGTH

Compound	Aging	Kg. per sq. cm. at optimum		
		Red	Yellow	Blue
ACS 1 pure-gum	Before	22.5	23.3	34.6
	After	30.6	34.4	42.0
MPC/MBT tread	Before	67	70	113
	After	121	103	148
HAF/RF1 tread	Before	95	106	110
	After	79	65	82
SRF/RF1 sidewall	Before	79	91	108
	After	79	79	84
MPC/DPG tread	Before	122	119	142
	After	44	44	47
HAF/DPG tread	Before	112	108	120
	After	31	30	38

crack growth, and that Blue and Yellow rubbers do not behave consistently in the different compounds in both initiation and propagation stages. Only in the sidewall SRF compound are the results completely in accord with technical classification.

No material was available for tests in DPG compounds, and, for the same reason, aging of the MPC compound only was possible.

The aged results show little alteration of the rates at a marked undercure, but great acceleration at longer cures; no optimum was reached in 120 minutes.

TABLE 11
CRACK GROWTH

Compound	Aging	Crack growth (mm.)	Kc. at optimum cure		
			Red	Yellow	Blue
MPC/MBT tread	Unaged	1-3	2.0	2.8	2.5
		3-7	9.8	6.2	8.5
	Aged	1-3	1.2	1.3	1.0
		3-7	4.6	3.5	2.4
HAF/RF1 tread	Unaged	1-3	2.8	2.7	3.0
		3-7	18.9	11.0	14.5
SRF/RF1 sidewall	Unaged	1-3	4.8	4.7	4.0
		3-7	8.9	7.9	6.7

Red, Yellow, and Blue rubbers are well differentiated in the order of increasing rate of crack growth.

ABRASION

Red, Yellow, and Blue rubbers were compared in an MPC tread under the conditions of low and high thrust given in the Appendix. No tests in other compounds were possible for lack of material. The tests were made on unaged and aged test-pieces at 60- and 40-minute cures, respectively. Average values, being means of results on three unaged, and of four aged test pieces, are given in Table 12.

TABLE 12
MPC/MBT TREAD
Modified Akron-Croydon abrasion ml./1000 rev. loss

Thrust (lb.)	Aging	Cure (min.)	Red	Yellow	Blue
10	Before	60	0.78	0.74	0.70
	After	40	0.75	0.76	0.71
45	Before	60	1.68	1.68	1.61
	After	40	1.79	1.84	1.86

The differences between the rubbers are small, the advantage lying with Blue rubber, except for the aged results at high thrust.

TIME TO REACH OPTIMUM PROPERTIES

It is well known that different manufacturers have different ideas about what constitutes a good technical cure. This is not surprising, since the optimum cure for one property may be very different from that of another, and the relative importance of any property depends on the purpose for which an article is to be used. The optimum for tear occurs earlier than the optimum for tensile strength, and if a period of aging is to be allowed, it occurs earlier still. Some

technologists prefer to use tear strength as a guide to a good technical cure, in which case it could be argued that a good technical cure for the ACS 1 compound is about 20 minutes at 140° C. The fact that a longer period is used for technical classification purposes is not of importance, since it has little effect on the relative differences between rubbers and is believed to discriminate more sharply between rubbers than shorter cures.

In many cases the property/time-of-cure curves tend to reach optimum values at ill-defined times, the so-called plateau effect. For this reason time-comparisons between Red, Yellow and Blue rubbers have been made at a fixed proportion of the optimum value, the exact percentage depending on the property under consideration. In all cases, this percentage was so adjusted that the comparisons were made on the well-defined rising portion of the property/time curve. In the case of tensile strength, modulus, and tear strength,

TABLE 13
QUALITATIVE ASSESSMENT OF TIME TO REACH A FIXED PROPORTION
OF THE OPTIMUM VALUE

1 earlier than 2; 2 earlier than 3; difference 20 per cent or more; Aged assessment in brackets; N, no assessment possible for all three rubbers in the test; NT no test

Compound	Rubber	T.S.	M	Tear	R	H	C.G.
ACS 1	R	3 (1)	3 (2)	3 (2)	3 (3)	3 (3)	3 (3)
	Y	2 (1)	2 (2)	2 (2)	2 (2)	2 (2)	2 (2)
	B	1 (1)	1 (1)	1 (1)	1 (1)	1 (1)	1 (1)
M ^c C/MBT tread	R	1 (2)	2 (1)	1 (2)	2 (N)	2 (1)	1 (N)
	Y	1 (1)	1 (1)	1 (1)	1	1 (1)	1
	B	1 (1)	1 (1)	1 (1)	2	1 (1)	1
HAF/RF1 tread	R	2 (N)	2 (2)	2 (2)	1 (2)	2 (2)	1 (NT)
	Y	1	1 (1)	2 (2)	1 (1)	1 (1)	2
	B	2	1 (1)	1 (1)	1 (1)	1 (1)	1
SRF/RF1 sidewall	R	2 (N)	2 (2)	3 (3)	2 (2)	2 (2)	2 (NT)
	Y	2	1 (1)	2 (2)	1 (1)	1 (1)	1
	B	1	1 (1)	1 (1)	1 (1)	1 (1)	2
MPC/DPG tread	R	1 (2)	2 (2)	2 (1)	2 (2)	2 (2)	
	Y	1 (1)	1 (1)	1 (1)	2 (N)	1 (3)	NT
	B	1 (1)	1 (2)	1 (2)	1 (1)	1 (1)	
HAF/DPG tread	R	2	2 (2)	2 (3)	2 (1)	1 (2)	
	Y	2 (N)	1 (1)	1 (2)	1 (3)	1 (1)	NT
	B	1	2 (2)	1 (1)	1 (2)	1 (1)	

a value of 90 per cent of the optimum was chosen, for resilience and hardness 95 per cent, and for crack growth 80 per cent. In making the assessments consideration was given to the fit of the curve to the experimental points, and the times so obtained have been converted to qualitative rankings 1, 2, 3 in such a manner that no difference between rubbers have been indicated unless it is of the order of a 20 per cent difference in curing time.

It is felt that this procedure indicates fairly those differences which are of practical importance, although, in many instances where a similar ranking has been given because the difference is less than 20 per cent, the differences are in the order of technical classification.

In the ACS 1 compound, the time differences between Red and Blue rubbers given in Table 13 are of the order of 100 per cent, with Yellow rubber intermediate, for all properties examined. One consequence of this observation is that a technical classification test need only be judged on its ability to discriminate between rubbers, its convenience and cost, and, of the possible alternatives to modulus in this connection, a hardness test is the most promising.

In the black compounds the greatest differences (up to 75 per cent) are shown in the SRF sidewall compound; in the tread compounds differences do not exceed 50 per cent, and rankings are either 1 or 2. The general trend is the same in all five compounds, the DPG compounds presenting only minor points of difference.

In the 28 sets of rankings shown in Table 13 for the unaged black compounds, Red, Yellow, and Blue rubbers are judged equal in six sets. In the remaining 22 sets, Blue rubber is ranked as 1 in 19 cases and Red as 2 in 21 cases. Yellow rubber tends more to the Blue than Red, and is graded as 1 on 17 occasions.

The rankings of Blue and Yellow rubbers are each altered by aging on three occasions; for Red rubber on aging a ranking of 1 becomes 2 on five occasions, and 2 becomes 1 on 4 occasions.

TABLE 14
TIME TO REACH A FIXED VALUE

1 earlier than 2; 2 earlier than 3
(Aged assessments in brackets; N, no assessment possible; (1) indicates no differentiation between RYB; NT, no test)

Compound	Rubber	T.S.	M	E	Tear	R	H	C.G.
ACS 1	R	3 (3)	3 (3)	3 (3)	3 (3)	3 (3)	3 (3)	3 (3)
	Y	2 (2)	2 (2)	2 (2)	2 (2)	2 (2)	2 (2)	2 (2)
	B	1 (1)	1 (1)	1 (1)	1 (1)	1 (1)	1 (1)	1 (1)
MPC/MBT tread	R	3 (N)	2 (2)	2 (1)	2 (2)	2 (N)	2 (1)	2 (3)
	Y	2	1 (2)	1	2 (3)	2	1	2 (2)
	B	1	1 (1)	2	1 (1)	1	1	1 (1)
HAF/RF1 tread	R	2 (N)	2 (3)	1 (1)	3 (2)	3 (3)	3 (3)	3 (NT)
	Y	2	1 (2)	1	2 (1)	2 (2)	2 (2)	2
	B	1	1 (1)	1	1 (1)	1 (1)	1 (1)	1
SRF/RF1 sidewall	R	3 (N)	2 (3)	3 (1)	3 (2)	3 (2)	2 (3)	3 (NT)
	Y	2	1 (2)	1	2 (3)	2 (N)	1 (2)	2
	B	1	1 (1)	2	1 (1)	1 (1)	1 (1)	1
MPC/DPG tread	R	3 (N)	2 (1)	1 (1)	3 (N)	2 (N)	2 (1)	NT
	Y	2	1	1	2	3 (2)	1 (1)	
	B	1	1	1	1	1 (1)	2 (2)	
HAF/DPG tread	R	1 (N)	1 (1)	2 (1)	2 (2)	N (N)	1 (1)	NT
	Y	1	1	1	2 (2)	2 (2)	1	
	B	1	2	2	1 (1)	1 (1)	1	

The technical classification grading is, therefore, maintained almost completely for Red and Blue rubbers in tread and sidewall type compounds containing acidic or basic accelerators, with Yellow rubber tending to behave more like Blue than Red. This overall picture is practically unaltered by a short period of oven aging.

TIME TO REACH A FIXED VALUE LESS THAN THE OPTIMUM

The time to reach a fixed value less than the optimum has also been assessed by a series of qualitative rankings, 1, 2, 3. In this case no precise standards of judgment were laid down, but consideration was given to the relative positions of the rising portions of the property/time curves. Crossings over of the Red, Yellow, and Blue curves in the early stages are rare occurrences, and nearly all the assessments were free from this complication. In all cases the rankings 1, 2, 3 represent substantial differences in curing time and there are a number of

TABLE 15
GRADE ONE AND OFF GRADE RUBBERS AT A FIXED CURE NEAR THE OPTIMUM FOR TENSILE STRENGTH

Type of compound	MPC tread						HAF tread					
	Visual grade			Off grade			First grade			Off grade		
	Red	Yellow	Blue	Red	Yellow	Blue	Red	Yellow	Blue	Red	Yellow	Blue
T.C. grade												
No. of samples	5	3	3	Nil	4	4	3	3	3	2	4	4
ASC 1 strain (%)	98	78	63	—	80	65	97	78	63	87	77	65
Tensile strength (kg./cm. ²)	175	189	199	—	153	177	190	196	210	185	201	206
300% Modulus (kg./cm. ²)	88	98	102	—	80	88	124	138	149	125	133	137
Elongation at break (%)	478	469	475	—	461	480	404	392	393	395	408	411
Resilience at 70° C (%)	57.5	58.4	60.0	—	56.3	57.2	66.6	67.0	68.3	68.1	66.1	68.4
Hardness (° B.S.)	65.7	67.7	68.9	—	64.1	66.8	62.4	65.4	67.5	63.7	65.0	66.5
Tear strength (kg./cm. ²)	61	60	93	—	45	76	94	98	118	87	98	109
Crack growth (cc.):												
1-3 mm.	3.8	7.4	6.0	—	3.0	3.2	7.8	5.8	3.2	6.5	6.5	5.6
3-7 mm.	24.9	26.6	21.7	—	21.2	24.4	24.9	20.2	12.0	25.2	22.8	19.7
Mooney scorch (min.)	27.2	29.2	26.3	—	24.6	24.0	25.9	22.4	22.1	22.4	23.0	22.7
Mooney cure rate (25/T25)	3.01	3.47	3.84	—	2.70	3.22	2.42	2.78	3.37	2.67	2.90	3.04

cases where the Red optimum value is so much below Blue that the time differences, based on a little less than the Red optimum, become very great indeed.

The assessments for time to reach a fixed value are given in Table 15 for both unaged and aged samples. In general, the effect is to exaggerate the differences noted in the preceding section. In the ACS 1 compound, cure times to reach a value a little short of the Red optimum differ by several hundreds per cent, and even in black compounds the differences sometimes exceed one hundred per cent.

Aging tends to change the picture only in points of detail, sometimes exaggerating sometimes smoothing the differences between Red and Blue, but leaving the general picture substantially the same.

ADDITIONAL TECHNICALLY CLASSIFIED RUBBERS

As a corollary to the preceding investigation of single bales of technically classified RSS 1, a limited amount of information has been obtained on 28 other technically classified samples, including RSS 1, 2 and 3, pale and brown crepes. The rubbers were used to prepare two compounds, viz., MPC and HAF treads (Nos. 2 and 3 of the Appendix), and, apart from the RSS 1 samples, a different set of rubbers was used for each compound, owing to lack of material. For the same reason, it was only possible to examine the rubbers for the range of properties used for the three RSS 1 bales by limiting the work to comparisons at a single cure period. This was chosen as 30' at 140° C, which the preceding investigation had shown to be approximately the cure for optimum tensile strength.

In Table 15 the results are given as averages for each T.C. grade, for off-grade and first-grade rubbers. The off-grades comprise the brown crepe, RSS 2 and RSS 3 samples, and the first grade include RSS 1 and pale crepes. Pale crepes are not normally used in carbon black compounds, but were included to make up the number of samples. Even so, no Red off-grade rubbers were available for test in the MPC compound.

Although the results are presented separately for first-grade and off-grade rubbers, it is not intended that they should be compared on technological grounds, since, in the assessment of off-grade rubber, much depends on other factors not taken into account here, such as degree of cleanness and degradation of the rubber hydrocarbon.

With a very few exceptions, the results confirm the maintenance of technical classification in the two compounds. In regard to vulcanizate properties, exceptions are crack growth and resilience. In all cases Mooney cure rate agrees with technical classification, whereas Mooney scorch rate is either less discriminating or anomalous.

CONCLUSIONS

Technically classified rubber is classified on its vulcanization characteristics, and these differences are not obscured when large loadings of carbon black are used, nor when different accelerators are employed.

The evidence obtained from the examination of three bales of technically classified RSS 1 support the general conclusion that, in all the compounds examined, whether pure-gum, tread, or sidewall, using MBT type accelerators, or DPG, whether tested soon after preparation of the vulcanizates or after aging, Blue rubber shows a generally higher level of properties than Yellow, which in turn shows a generally higher level of properties than Red. Blue rubber is

harder than the others and has a higher modulus, although this is not marked in tread compounds. It has a higher resilience, higher tensile strength, and higher tear strength. The disadvantages of Blue rubber are less resistant to scorching and to crack growth. In most instances Yellow rubber is intermediate between Blue and Red. There is no evidence of any marked difference between the rubbers in laboratory abrasion tests on MPC tread compounds.

The examination of a further 28 samples of technically classified first-grade and off-grade rubbers in two of the tread compounds at a single cure confirmed, with only a few exceptions, the maintenance of the technical classification.

SUMMARY

The history of the ACS 1 compound and its use by natural-rubber producers to assess the variability of plantation sheet and crepe is described. Using modulus at a fixed cure as a criterion of vulcanizing properties, the large variation found in the ACS 1 compound is greatly reduced by the addition of carbon black, but there is good correlation between moduli in the presence and in the absence of black.

Detailed results of tests for a range of properties are presented for Red, Yellow, and Blue technically classified rubber in compounds loaded with MPC, HAF, and SRF blacks, and with different accelerators. Some of these properties show a wider range of variation than modulus, and they also indicate that technical classification based on modulus in the ACS 1 compound is justified by the behavior of the black-loaded compounds, both in regard to the level of vulcanizate properties, curing times, and scorch characteristics.

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APPENDIX

Experimental procedure used in tests on technically classified rubbers:

	TEST FORMULAS					
	1	2	3	4	5	6
	ACS 1	MPC tread	HAF tread	SRF sidewall	MPC tread	HAF tread
Rubber	100	100	100	100	100	100
Zinc oxide	6	5	5	5	5	5
Sulfur	3.5	3	2.5	2.5	3	2.5
Stearic acid	0.5	2	2	2	2	2
M.B.T.	0.5	1	—	—	—	—
Santocure RF1	—	—	0.8	0.8	—	—
D.P.G.	—	—	—	—	1	0.8
MPC black (Micronex)	—	50	—	—	50	—
HAF black (Philblack O)	—	—	50	—	—	50
SRF black (Furnex)	—	—	—	30	—	—

Compounds were prepared on a 12 × 6 inch laboratory mill and in a K.O. Intermix. Intermix batches were used for crack growth tests; other properties were determined on mill mixed batches.

VULCANIZATION

Vulcanization was carried out in a laboratory 4 daylight platen press, fitted with automatic temperature control and with thermometers recording the temperatures of the individual platens.

Vulcanizing temperatures were 140° C for MBT and Santocure RF 1 and 148° C for DPG compounds.

Test specimens for each property were vulcanized over a wide range of cure periods between 10 and 160 minutes.

TESTING

Tensile strength, modulus, elongation at break were measured on 4-mm. thick Schopper rings, using a Goodbrand R5 dynamometer.

Resilience and *hardness* were measured on the inner Schopper disks from the tensile tests.

Hardness was measured on two plied up disks, with a Wallace dead load hardness gauge reading directly in degrees B.S.

Resilience was determined with the Dunlop tripsometer, with the specimen holder modified to take the inner Schopper disk in place of the normal 8 × 8 × 4 mm. test-piece. Other modifications to the machine include the application of suction to the back of the specimen holder, which eliminates the necessity to apply a correction for block shuffle of the specimen during impact; more accurate setting of the initial angle by means of an adjustable stop fitted to the scale, and of the rebound angle by a vernier fitted to the revolving steel disk; automatic release of the pendulum without impulse effects by means of an electrically operated solenoid brake.

Further batches of compounds were prepared for the determination of *tear strength* according to B.S. 903 conditions.

CRACK GROWTH

In carrying out de Mattia crack growth tests on the carbon black compounds, consideration was given to recent published work on the subject, particularly by Buist¹⁶. In addition, a knowledge of the trend of development of the ISO conditions of test led to the adoption of a 3-inch free length of specimen; otherwise, B.S. 903 conditions of operation were used. The crack was initiated by piercing the specimen with a 1 mm. spear probe in a jig constructed in the laboratory workshop.

When the length of crack is plotted against the number of kilocycles of flexing, the curve is usually more or less sharply rising during the first one or two mm. extension of the crack, followed by an approximately linear propagation. Deviations from this generalized picture have been noted (1) in the case of SRF black sidewall compounds, which gave curves linear from the commencement, and (2) in certain cases, a linear propagation portion, followed by an accelerated rate of crack growth. Type (2) curves occur in certain circumstances, e.g., when isolated fatigue cracks merge into the main crack.

In Table 11, the results for optimum rate of crack growth are expressed in terms of kilocycles for the crack to extend from (1) 1 to 3 mm., (2) 3-7 mm. Rates of this order of magnitude are in keeping with the figure of 5.65 kc. given by Buist¹⁶ for the crack to grow to 8 mm. in a natural-rubber channel black tread vulcanizate containing no antioxidant.

Abrasion resistance was determined on the Akron-Croydon machine.

Recent work in the LAC laboratories has indicated that Akron-Croydon abrasion tests often approach more nearly to known road ratings when the thrust on the test wheel is greatly increased over the normal B.S. 903 conditions, e.g., 45 lb. instead of 10 lb.; a further small improvement is effected if the angle of contact of the abrasive wheel is increased to 20°.

Aging tests were carried out in an air oven kept at 70° C, on test-pieces from a range of cure periods selected so as to give optima in the property-time curves after aging. The aging period was 4 days.

MOONEY SCORCH PROPERTIES

The unvulcanized compounded stocks were tested in a Mooney viscometer kept at 121° C, as indicated by thermometers set in the platens.

Measurements were made of the time required to reach 5 units above the minimum in the viscosity-time curve, the *scorch time*, and also of that required to reach 30 units above the minimum. The difference (T25) between this figure and the scorch time, when divided into 25, was used as an index of the *cure rate* (25/T25), in Mooney units per minute.

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THE MOONEY VISCOMETER *

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PREPARATION OF THE TEST-SPECIMENS

The preparation and forming of test-specimens for the Mooney viscometer by compression between the stator and rotor is accomplished in a rather crude way, and certainly more care should be taken than is evidently considered necessary. Investigations have shown that, by the use of pieces of rubber stock of as nearly the same size as possible as the cavity between the stator and rotor, several sources of error and certainly disturbing factors can be avoided, or at least minimized. As a good example of such errors are the considerable internal stresses which affect the measurements.

In Figure 1, the effects caused by internal stresses, which, after completion of a test and removal of the specimen from the rotor, cause shrinkage and swell-

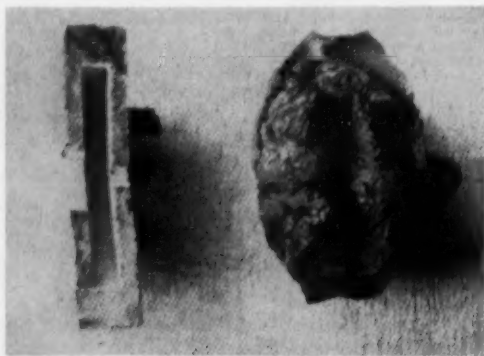


FIG. 1.

ing, are easily recognizable by a comparison, to scale, with a vulcanized specimen whose cross-section is the same as that of the unvulcanized specimen as it fills the cavity between the rotor and stator. The internal stresses result in a hardening of the test-specimen, which may increase the true Mooney viscosity by as much as 5 per cent.

Information available in written instructions how to operate the viscometer, and in the literature concerning the time of preheating the test-specimen and the time that the rotor should be operated before a final reading is made or a

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Kautschuk und Gummi*, Vol. 7, No. 11, pages WT 263-265, November 1954. This is a much shortened version of a report presented at the meeting of the German Rubber Society in Goslar, May 1953, and compares the operation and experimental results obtained with the Mooney viscometer and the Defo apparatus. The twenty-two pages and numerous illustrations of the original paper have been condensed to give the most important findings, and a description of the apparatus and its operation is omitted on the assumption that this is too well known to warrant inclusion.

constant reading is attained, is very indefinite and in some cases so impracticable, particularly with respect to consistent results, that one is confronted with the choice of two possible methods of operation. The first is to choose, for the particular material being tested, an arbitrary time of preheating and time of operating the rotor to approximately constant reading and then make a final measurement. This obviously means that any comparison of the values obtained with different materials is impracticable. The alternative is to disre-



FIG. 2.

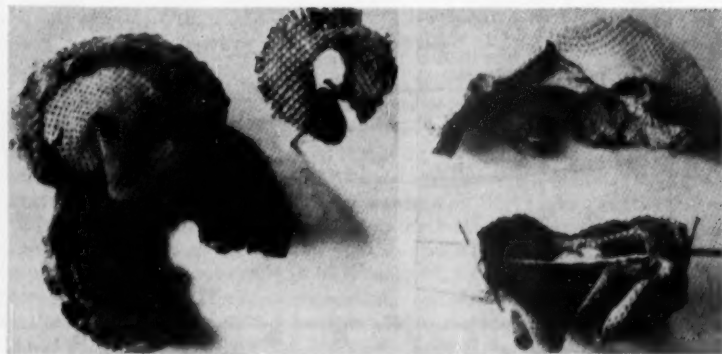


FIG. 3.

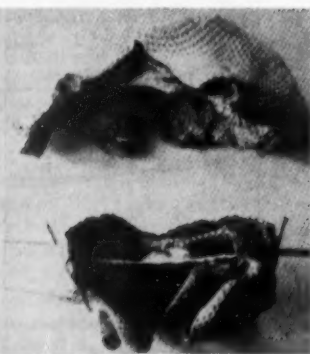


FIG. 4.

gard whether the test-specimen is heated sufficiently or whether a constant reading has been attained during the operation of the rotor, and to choose arbitrarily a preheating time of 1 minute. After operation of the rotor for 4 minutes, the final measurement is made, regardless of the course of the time-viscosity curve.

This latter method seems to be the one which is most widely used. In the original work, of which the present paper is a much condensed version, the difficulties which are encountered in the use of both the methods described above are discussed at length.

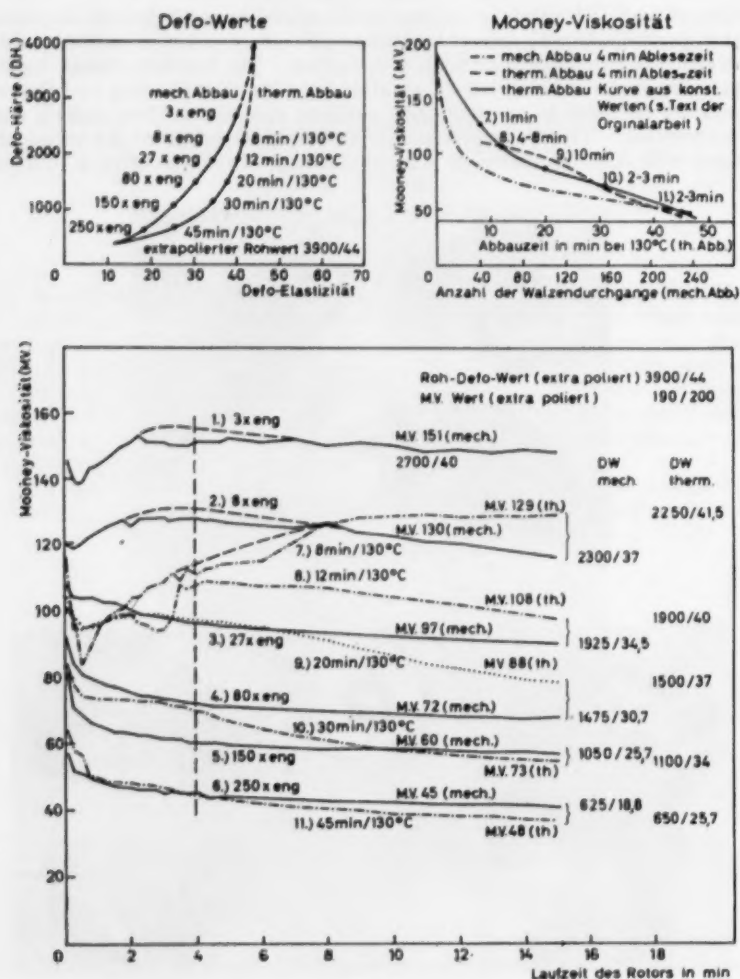


FIG. 5.

Top right-hand diagram

Lower abscissa

Upper abscissa

Ordinate

Legends on diagram

Number of passes through a mill for mechanical breakdown.

Time in minutes at 130°C for thermal degradation.

Mooney viscosity (M.V.)

Top left-hand diagram

Abscissa

Ordinate

Left-hand curve

Right-hand curve

Legend above abscissa

Defo elasticity.

Defo hardness.

Mechanical breakdown.

Thermal degradation.

Extrapolated initial hardness 3900.

Extrapolated initial elasticity 44.

Legend on left-hand curve

Number of passes through a tight laboratory mill.

Lower diagram

Abcissa

Ordinate

Upper right-hand legend

Fig. 5—Continued

Running time of rotor in minutes.

Mooney viscosity.

Initial Defo values (extrapolated).

Hardness 3900

Elasticity 44

Left-hand inner series (1-6) represents the number of passes through a tight mill.

The other legends are obvious.

BEHAVIOR DURING THE TEST PROCEDURE

With respect to the actual carrying out of the viscosity test, the following brief comments may be made.

(1) As soon as the rotor is started, shearing begins, and this separates the test-specimen into a stationary portion and another portion which turns with the rotor.

(2) Shearing takes place, as can be demonstrated, directly on the surface of the rotor, so that the layer which turns with the rotor consists only of material which is in the grooves of the rotor.

(3) A viscosity measurement is, then, conceivable only if, immediately after shearing, there is, between the stationary material and the material which turns with the rotor, a layer of material which bonds the stationary and rotating portions and which represents the only portion the viscosity of which is actually measured.

(4) This intermediate layer is naturally not always present, as is evident by examination of test-specimens at the end of the test.

(5) Depending on the particular material, this intermediate layer is often only temporary, i.e., it may alternate with relatively short or long periods of complete separation.

This behavior is shown clearly in Figures 2, 3, and 4.

Figure 2 shows how the bed of rubber stock in the grooves of the rotor has been separated by the shearing action, and how, during operation of the rotor, it again bonds only very loosely with the stationary portion of the rubber stock. Part of the material in the rotor is, therefore, left behind adhering to the rotor when the test-specimen is removed from the rotor. In such cases, therefore, only an intermediate stage between viscosity and friction is measured.

Figures 3 and 4 illustrate cases where the stationary layer and the layer of material rotated by shearing have remained separated. Figure 3 represents a sample of reclaimed rubber. In this case, only the friction between the two layers is measured. The Mooney viscosity values of materials of this kind are, therefore, much too low, as will be shown later in a comparison of the DH values of Defo tests and corresponding Mooney viscosity values.

Figure 4 represents a carbon black mixture which was tested for its tendency to scorch. It is evident that the same result was obtained as with the reclaimed rubber, because of the more elastic phase formed as a result of incipient vulcanization. The danger of a permanent separation of layers in the test-specimen must always be faced in tests of scorching, if the test is carried to any considerable degree beyond the point of incipient vulcanization. From this point of view, it is easy to explain the fact that any test method for determining scorching by the Mooney viscometer must be restricted to determinations of the first indication of such a change.

From this rather brief summary and discussion, it may be concluded that accurate viscosity measurements by the Mooney apparatus can be made only with materials whose behavior conforms to the requirements of point (3) above.

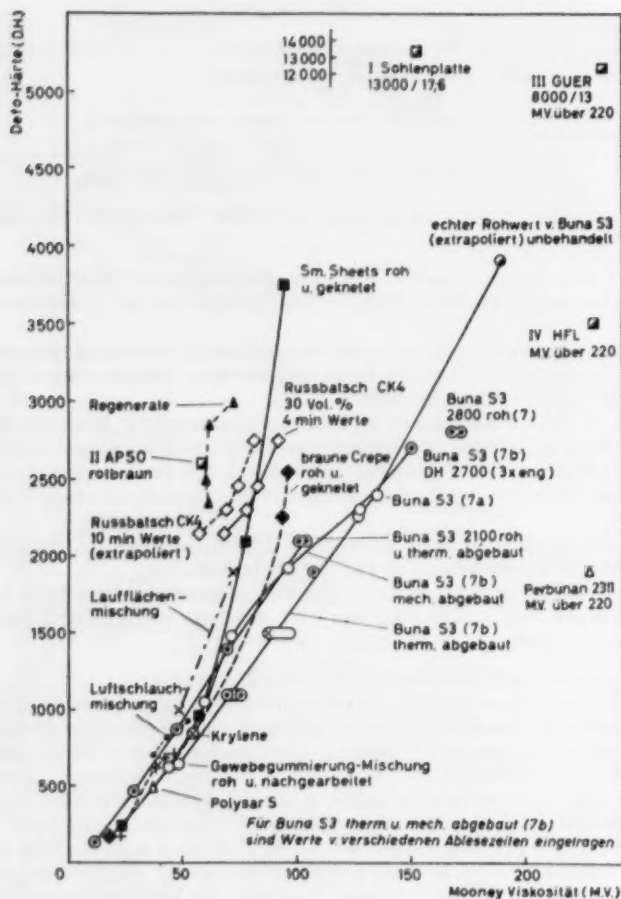


Fig. 6.

- Abcissa
Ordinate
Within the diagram
- Left-hand column..... Reclaimed rubber.
II AP50 (red-brown).
Carbon black batch (extrapolated to 10 min.).
Tire-tread mixture.
Inner-tube mixture.
- Second column..... Smoked sheet (untreated and masticated).
Carbon black batch CK4 (30 vol.-%; 4 min.).
Brown crepe (untreated and masticated).
Krylene.
Rubber fabric formulation.
Polysar-8.
For Buna-S, both thermally degraded and mechanically broken down (7b) values for different times are recorded.
- Third column..... Sheet soling I 13,000/17.6
True initial (extrapolated) value of untreated Buna-S3.
Buna-S3. Initial untreated 2800 (7).
Buna-S3 (7b). Defo hardness 2700 (3 passes through a tight mill).
Buna-S3 (7a).
Buna-S3 initially 2100 and thermally degraded.
- Mooney viscosity.
Defo hardness.

FIG. 6—Continued

Buna-S3 (7b) mechanically broken down.
 Buna-S3 (7b) thermally degraded.
 Fourth (right-hand) column
 GUER 8000/13, Mooney viscosity above 220.
 HFL IV, Mooney viscosity above 220.
 Perbunan-2311, Mooney viscosity above 220.

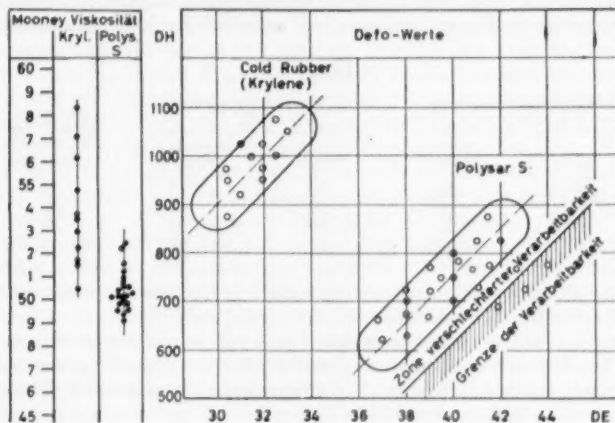


FIG. 7.

Right-hand diagram Heading Defo values
 Two legends in lower right-hand part of diagram
 Upper legend
 Zone of impaired processability.
 Lower legend
 Limiting range of good processability.

RESULTS OF THE INVESTIGATION

A discussion of the results of the Mooney viscosity measurements must be limited in this condensed version of the complete investigation to three graphs, represented in Figures 5, 6, and 7, which best illustrate the most important results of the work.

In one series of experiments, evidence was obtained that, in contrast to the resistance to deformation (DH) in the Defo test, a factor must be included which, in parallel with the varying high-elastic deformed component (DE) in the Defo test, may be large or small. However, in Mooney viscosity measurements, it is impossible to distinguish this factor and to differentiate it from the integral value. By the comparison of the Defo test and the Mooney viscosity test described in the present work, a way is shown how to separate Mooney viscosity values into a factor which represents the resistance to deformation (DH) of the Defo test and a second factor which represents the elastic deformation factor (DE) of the Defo test.

A particularly good example of this is the comparison of the Defo and Mooney viscosity values of thermally degraded and mechanically broken-down Buna-S rubber, shown in Figure 5.

The Defo test shows, as is known, that Buna-S3, when degraded thermally to a given DH value, has a higher DE value than the same rubber broken down mechanically to the same DH value. The conclusion therefore seems warranted that, if in a Mooney apparatus, higher viscosity values are found for thermally degraded Buna-S3 than for mechanically broken down Buna-S3, the difference

in the values corresponds to the higher DE value of the thermally degraded Buna-S3.

The differences in the Mooney viscosity values, derived from Figure 5 for rubber thermally degraded and mechanically broken down to the same DH value, are itemized in Table I.

In a more extensive evaluation of the curves in Figure 5, for which the original complete work must be consulted, serious difficulties were encountered,

TABLE I

Mechanical break-down on a tight laboratory mill		Thermal degradation at 130° C		Difference between the two methods Mooney units
Passes	Mooney viscosity	Minutes	Mooney viscosity	
50	82	10	115	33
100	69	20	89	20
150	60	30	70	10
200	53	40	57	4

particularly the difficulty of obtaining satisfactorily precise measurements in the Mooney viscometer with thermally degraded rubber.

The proof that the elastic component of a rubber plays a part in measurements by the Mooney viscometer and represents a corresponding fraction of the viscosity value is also made evident by the comparative data on DH values and Mooney viscosity values recorded in Figure 6.

If, for example, one examines which Mooney values of smoked sheet, brown

TABLE II

Rubber	DH value	DE value	Mooney viscosity
Smoked sheet	2250	35.2	80
Brown crepe	2250	38	95
Buna-S3 (thermally degraded)	2250	41.5	128

crepe, and Buna-S3 correspond to the Defo DH value of 2250, it will be seen that the Mooney values represent a graduated series corresponding to the Defo DE values (see Table II).

That the Mooney viscosity values of the three rubbers recorded in Table 2 differ so greatly can probably be explained, not only by the elastic component as a factor in the integral Mooney values, but also by the fact that a given DH value, for example, 1000 DH units (g), does not always correspond directly to

TABLE III

DH values between	Smoked sheet Mooney value	Brown crepe Mooney value	Buna-S3 Mooney value
0 and 1000	58	62	66
2000 and 3000	11	13	42

the same Mooney viscosity value. Table III gives representative data on this point.

The characteristics evident from the data in Table III show that this behavior of rubber is an obstacle in any comparison of Mooney viscosity values, not only of different rubbers, but even of the same rubber degraded or broken down to different degrees. A further conclusion which might be drawn from the data is that, where Mooney viscosity data are lacking, conversion of Defo

DH values into Mooney values, and vice versa, would seem to be possible only when standard curves of comparison are available for every individual case.

The fact that the Mooney viscosity values include an apparently important factor representing the elastic component of the rubber properties probably serves to explain the lack of agreement in the published literature, because different rubbers or rubber mixtures of the same Mooney viscosity may in one case show good and in another case bad processing characteristics. Figure 7 shows a representative case of this kind for Krylene and Polysar-S.

As is evident in Figure 7, a whole series of similar Mooney values were obtained, in spite of the fact that the two types of rubber show considerably different processing characteristics, with Krylene showing, as is known, the better processibility. We are, therefore, confronted with the fact that, even when Mooney viscosity values are the same, great differences in processing characteristics may be found. The Defo DH/DE values show why this is true. High DH values with low DE values, exemplified by Krylene, are reflected in better processibility than are low DH values and high DE values.

In other words, materials showing high DH values and low DE values and, conversely, materials whose DH values are low and whose DE values are high, may, because of differing proportions in the Mooney viscosity values of the component corresponding to the elastic deformation factor in the Defo values, show the same Mooney viscosity values. In this case, the sums of the two factors which together make up the Mooney viscosity values are the same and, therefore, the latter values are the same.

The lack of any possibility of measuring, by the Mooney viscometer, the elastic component can, therefore, result in misleading data. Whether measurement of recovery values in the Mooney viscometer are of any help in this respect is still an unsolved problem. Special experiments to throw light on this problem with the standard instrument available were not possible, since this particular instrument is not equipped with the devices necessary for such measurements.

The complete investigation, which the present paper describes in greatly condensed form, shows clearly how indispensable it is for any instrument to give measurements of the elastic deformation which parallel results in the factory if the measurements are to be expected to indicate the processability of the material in question.

FREE-RADICAL ACTIVITY OF REINFORCING RUBBER FILLERS *

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In our studies of the mechanism of rubber reinforcement, we were led to assume that primary valency bonds are likely to form between an "active" filler and the rubber-matrix via free-radical intermediates. The hypothesis was based on the following considerations.

(1) Although a strong school of thought still maintains that the strength of bonding depends mainly on van der Waals forces, and therefore on particle size¹, a number of individual observations suggest the presence of "reactive sites" and formation of strong bonds of a chemical nature between filler and rubber². Foremost among these is the phenomenon that the incorporation of active pigments such as carbon blacks, silicas and the like into rubber results in the insolubilization of a part of the rubber³. This part is conveniently called "bound rubber" or "carbon-gel".

(2) Farmer and his school have shown that the vulcanization process is based on a free-radical mechanism, wherein a number of the rubber double-bonds and α -methylene groups, sulfur and accelerator are involved, resulting in the formation of three-dimensional giant networks⁴. The mechanism of mastication is also known to consist of the production of free radicals in the presence of suitable 'radical acceptors', such as oxygen⁵.

(3) There are some common features in both reinforcement and vulcanization, such as crystallization effects⁶.

(4) Little or no reinforcing action of otherwise active pigments is observed with saturated polymers, for example, polyisobutylene⁷.

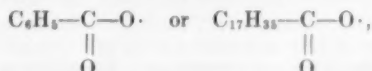
Correlation of these facts appeared most plausible if we assumed that the formation of chemical bonds between pigment and rubber constitutes an integral part of the chemical cross-linking that may commence in the rubber mill and be completed by vulcanization, all the interacting partners exhibiting free-radical character at one stage or the other. To test this hypothesis, we have studied the reactivity of pigment surfaces towards simple organic and inorganic free radicals. Controls with the corresponding ionic species were included to ensure that the effects observed were due to free-radical reactions.

Although the results will prove of particular interest in the rubber field, they are also likely to throw new light on the problem of chemisorption and also, perhaps, on the nature of catalytic activity of some solids of interest in other fields. The results are briefly as follows.

Active pigments react with free radicals, with the formation of new primary valency bonds. Thus, certain reinforcing blacks can, by the attachment of $\text{SO}_2^{\cdot -}$ free radical ions, be made hydrophilic; they are easily dispersed in water to form stable colloidal suspensions.

* Reprinted from *Nature*, Vol. 173, pages 997-998 (1954).

Introduction of organic free radicals, such as



yields chemically modified pigments, showing markedly changed dispersion and wetting characteristics in various solvents.

Monoxidation products of certain diamines, such as benzidine blue derived from benzidine, being semiquinones in character, easily react even with less-active pigments (for example, silicas) and thus provide a useful measure of activity.

From the experiments with free radicals, the number of active centers for a series of fillers has been calculated and found to cover a range of 0.01–2.3 per 100 sq. Å.

Multifunctional organic free radicals, such as polystyrene diradicals, as may be set up in the course of uncatalyzed mass polymerization at moderate temperature, on reaction with active carbon blacks, form cross-linked electrically conducting gels, which resist solvent extraction. These are considered to be complete analogs of the well-known rubber-carbon gels. The mechanism of their formation, namely, by a free radical reaction, is strongly supported by the lack of gel formation if polystyrene granules are dissolved and an active pigment is added to the solution.

Oxidation reactions of pigment surfaces at temperatures of 50–70° C were studied by the well-known Russell technique. Exposure of photographic emulsions to pigments gave results of a very complex nature. By using suitable screening agents, we have been able to detect at least three different effects: (1) luminescence, (2) a pseudo-photographic effect as produced by oxidizing agents, hydrogen peroxide being the most common fog-producing material, and (3) an emission. From the evidence obtained so far, the last is considered to consist of low-energy electrons (probably less than 10 eV.) that are made available by an oxidation mechanism comparable to the Kramer effect with freshly abraded metal surfaces.

Pigments of comparable particle-size are not equally active towards free radicals. The photographic results also show pronounced differentiation as regards ability of different pigment surfaces to affect photographic emulsions. It therefore appears that small particle-size of a pigment is a necessary, though not sufficient, condition for activity.

The evidence obtained seems sufficient to suggest that reinforcing blacks and also a number of inorganic active fillers can act as single-electron donors and can, in the presence of radicals or radical acceptors, produce chemically modified solids by the formation of new primary valence bonds. It furthermore would appear worth while to investigate the actinic effects of free radicals generally, since, in a way, they may be regarded as single electrons attached to material particles.

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- ² Stearns and Johnson, *Ind. Eng. Chem.* **43**, 146 (1951).
- ³ See, for example, Sweitzer, *Rubber Age* (N. Y.) **72**, 55 (1952).
- ⁴ Farmer and Shipley, *J. Polymer Sci.* **1**, 293 (1946), and earlier papers.
- ⁵ Pike and Watson, *J. Polymer Sci.* **9**, 229 (1952).
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CHLORINATION OF NATURAL RUBBER SOLUTIONS BY MEANS OF PHENYL IODODICHLORIDE *

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In a previous communication¹ it was shown that chlorination of natural rubber by means of gaseous chlorine proceeds by four stages, the predominant reaction being substitution of chlorine, with attendant cyclization. It was considered that similar studies with a reagent reported to be an additive chlorinating agent, would be complimentary to the previous investigation. Garvey, Halley, and Allen² have demonstrated the use of aryl iododihalides as chlorinating agents for olefinic compounds. Bloomfield³ has utilized phenyl iododichloride to prepare the additive dichloride from purified oxygen free rubber hydrocarbon. He has reported the reaction to be additive to the extent of 96 percent; however, considerable substitution took place when the reaction was carried out in presence of quinol. The present investigation deals with the reaction of pale crepe and deproteinized rubbers with varying proportions of phenyl iododichloride. The loss of double bonds with the incorporation of chlorine into the rubber molecule was followed by the quantitative ozonization of the products. Hydrogen chloride evolved during the preparation of the partially chlorinated products was also determined.

The chlorinated pale crepe rubber having a chlorine content of 50.6 per cent was again subjected to an after-chlorination with gaseous chlorine to yield a product of 73.6 per cent chlorine content.

EXPERIMENTAL

RUBBER SOLUTION

(1) *Pale crepe*.—For the work on chlorination of pale crepe rubber, 4 per cent pale crepe rubber solution in carbon tetrachloride was used. For studies on hydrogen chloride evolution, the method described in (2) was followed.

(2) *Deproteinized rubber*.—Known weights of deproteinized rubber prepared according to the method of Noble⁴ were taken in reaction flasks and carbon tetrachloride (70 cc.) was added to each of the flasks and the mixture left over till homogeneous solutions were obtained. Homogeneous solutions were obtained readily when the swollen mass was exposed to four or five hours of direct sunlight.

PHENYL IODODICHLORIDE

This reagent was prepared according to the method of Garvey, Halley, and Allen².

CHLORINATION

(1) *Pale crepe rubber*.—Ten-cc. portions of crepe rubber solutions were taken in reaction flasks, diluted with 60 cc. of carbon tetrachloride, and varying

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 30, No. 5, pages 129-137 October 1954.

known amounts of phenyl iododichloride were added to each. These mixtures were refluxed on a water bath and clear homogeneous solutions were obtained. The homogeneous solutions were then poured separately into ethyl alcohol. The product was pressed out to give a thin film which was dried in vacuum. The chlorine contents of the dried products were determined according to the method of Belcher and Godbert⁵. Products varying in chlorine contents from 2.5 to 50.6 per cent were thus obtained.

The chlorinated rubber of 50.6 per cent chlorine content, after being dispersed in carbon tetrachloride, was subjected to the action of gaseous chlorine, to obtain a product of 73.6 per cent chlorine content.

Hydrogen chloride evolved during the reaction was determined by carrying out another set of experiments, in which the rubber solution was prepared and chlorinated in several flasks as described below under deproteinized rubber. Results are given in Table 3.

TABLE 1
REACTION BETWEEN PHENYL IODODICHLORIDE AND
PALE CREPE RUBBER

Sample No.	Chlorine content (per cent)	Atoms chlorine per (C ₆ H ₅ Cl) ₂ 100	Theoretical chlorine content corresponding to column 3	Per cent hydrolysis products from corresponding ozonides expressed as -COOH	Number of double bonds lost per 100 C ₆ H ₅ units
1	<2.3	<5	<2.5	85.9	0.0
2	2.9	6	3.03	81.6	2.9
3	8.04	17	8.15	72.7	13.5
4	9.69	20	9.45	60.2	28.3
5	11.53	25	11.54	72.3	23.94
6	17.48	40	17.28	58.6	30.3
7	25.6	66	25.63	48.8	41.9
8	30.5	84	30.42	43.7	48.0
9	36.4	110	36.4	31.5	62.5
10	40.7	131	40.7	24.6	76.7
11	50.6	196	50.6	14.9	82.3
12	50.9	199	50.96	19.5	76.8
13*	59.5	281	59.5	18.1	78.4
14*	73.6	531	73.6	16.5	80.36

* Final chlorination of 50.6 per cent product by gaseous chlorine.

(2) *Deproteinized rubber*.—The flask containing the deproteinized rubber solution was fitted with a reflux condenser with an inlet tube for passing in nitrogen and an exit tube connecting to two absorption vessels. Known amounts of phenyl iododichloride were added, and a current of nitrogen which had been passed through alkaline pyrogallol and concentrated sulfuric acid was passed through the solution to flush out the air from the system. The reaction flask was heated, and the contents were refluxed to obtain a homogeneous solution, the passage of nitrogen being continued all the time. The flask and its contents were cooled under nitrogen. The exit gases from the reaction flask were bubbled through water in the absorption vessels to absorb any hydrogen chloride that may be liberated during the reaction.

The hydrogen chloride was determined by titrating the contents of the absorption vessels, and the results are given in Table 4. The chlorinated product was precipitated with ethyl alcohol and, after washing, was dried in vacuum and chlorine contents determined.

TABLE 2
REACTION BETWEEN PHENYL IODODICHLORIDE AND
DEPROTEINIZED RUBBER

Sample No.	Chlorine content (per cent)	Atoms chlorine per (C ₅ H ₇ Cl ₂)/100	Theoretical chlorine content corresponding to column 3	Per cent hydrolysis products expressed as -COOH	Number of double bonds lost per 100 C ₅ H ₈ units	Remarks
1	0	0	0	75.6	0	Deproteinized rubber alone. Fresh solution prepared for each experiment.
2	7.08	15	7.24	73.9	2.3	
3	8.65	18	8.49	68.4	9.5	
4	11.9	26	11.95	70.9	6.2	
5	15.3	35	15.44	59.3	21.6	
6	16.3	38	16.55	56.2	25.7	
7	30.07	82	29.97	33.8	55.3	
8	33.0	95	33.2	30.1	60.2	
9	41.5	136	41.5	16.7	77.9	
10	42.6	142	42.53	17.8	76.5	
11	43.4	147	43.43	16.7	84.9	
12	44.4	153	44.4	11.5	86.2	
13	46.48	166	46.4	13.7	81.9	
14	48.4	180	48.46	10.5	82.4	

QUANTITATIVE OZONIZATION

About 100 mg. of the chlorinated product was dispersed in carbon tetrachloride (70 cc.) and subjected to the action of ozonized oxygen. The resulting ozonide was hydrolyzed with water and, from the amounts of hydrolysis products obtained, the number of double bonds lost during chlorination was calculated, as described earlier¹. The results are tabulated in Tables 1 and 2 and graphically shown in Figure 1.

RESULTS AND DISCUSSION

Curve A, Figure 1 (Table 1) represents the loss of double bonds in pale crepe rubber on chlorination with phenyl iododichloride, measured by quantitative ozonization of the chlorinated samples. It is observed that, for the first 25 chlorine atoms introduced per 100 isoprenic units, about 23 double bonds are lost, i.e., approximately one double bond per chlorine atom. The next 105 chlorine atoms introduced per 100 isoprenic units cause a further decrease of about 53 double bonds, i.e., one double bond per two chlorine atoms. Thereafter, further introduction of chlorine atoms causes only a small loss in unsatu-

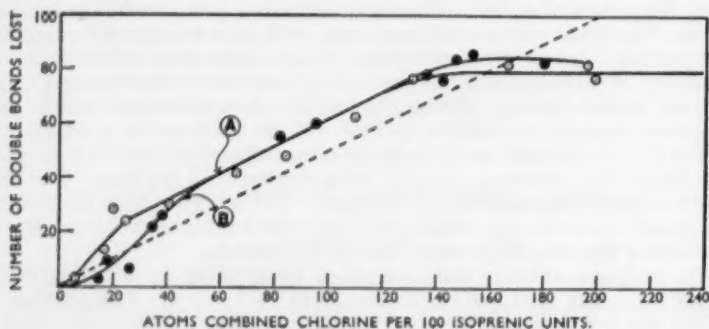


FIG. 1.

ration, and after 150 chlorine atoms per 100 isoprenic units, there is practically no change of unsaturation, even when 530 chlorine atoms per 100 isoprenic units are introduced by after chlorination of the 50.6 per cent product with gaseous chlorine. It is thus inferred that, up to the introduction of 25 chlorine atoms per 100 isoprenic units, cyclization reaction takes place accompanying either a substitutive attack (Equations 4, 5, 6) or an additive attack (Equations 7, 8, 9) by chlorine radicals (Equations 1 and 2) derived from the thermal decomposition⁶ of phenyl iododichloride.

The results of the hydrogen chloride determination at this stage reveal only 0.8 per cent hydrogen chloride on the weight of the rubber. If the reaction proceeds according to Equations 4, 5 and 6, the hydrogen chloride thus produced would have to be accounted for. The simplest way would to to assume that

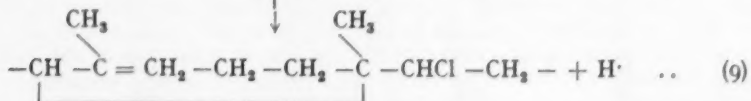
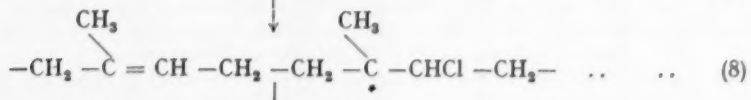
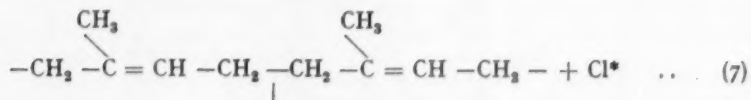
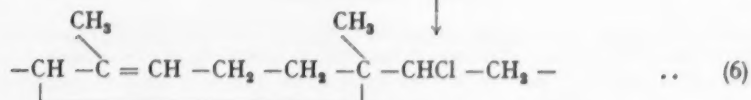
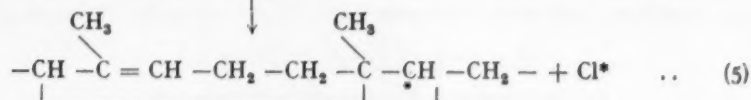
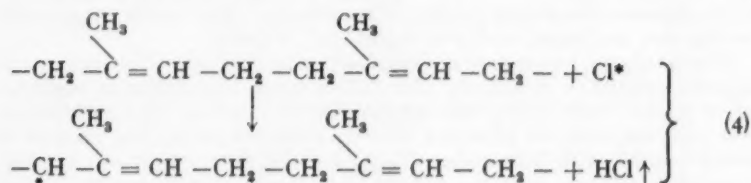
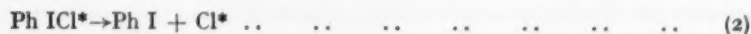


TABLE 3
REACTION BETWEEN PALE CREPE RUBBER AND PHENYL IODODICHLORIDE

Sample No.	Chlorine content (per cent)	Number of atoms of chlorine per 100 C ₆ H ₅ units	Per cent hydrogen chloride evolved on the weight of rubber
1	6.98	14	0.74
2	8.34	17	0.51
3	17.2	40	3.85
4	22.43	55	6.59
5	24.1	61	1.3
6	29.6	81	1.58
7	32.7	93	1.54
8	32.8	93	1.48
9	38.8	122	3.1
10	43.1	145	2.59
11	47.20	172	5.06

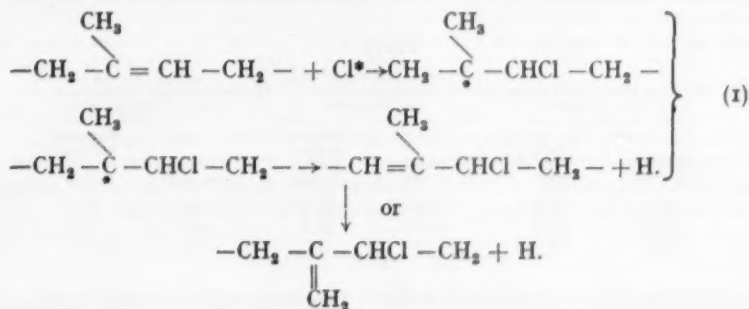
the hydrogen chloride thus produced adds to the double bond of the rubber and, hence, is not available for estimation. Since observations in this laboratory⁷ and elsewhere have shown that the reaction of hydrogen chloride with rubber has a negative temperature coefficient, it appears that the preceding explanation for the absence of hydrogen chloride is improbable. This leaves us only with the alternate mechanism shown in Equations 7, 8 and 9.

This is followed by a purely additive reaction of chlorine. The reaction subsequently follows an apparently substitutive course, since there is negligible loss of double bonds during this last stage of the reaction. It has, however, been observed that the hydrogen chloride evolution during the reaction of phenyl iododichloride with rubber (Tables 3 and 4) does not support a purely substitutive reaction, since the amount of hydrogen chloride evolved at any stage, except in a few cases, is between 0.5 to 3.5 per cent only. To account

TABLE 4
REACTION BETWEEN DEPROTEINIZED RUBBER AND PHENYL IODODICHLORIDE

Sample No.	Chlorine content (per cent)	Number of chlorine atoms per 100 C ₆ H ₅ units	Per cent hydrogen chloride evolved on the weight of rubber
1	7.3	15	0.86
2	7.5	16	0.86
3	15.3	35	0.58
4	25.12	64	5.24
5	30.1	82	1.1
6	32.9	95	2.03
7	33.3	95	1.8
8	34.2	100	1.16
9	34.45	101	2.05
10	35.3	105	9.6
11	38.6	120	1.9
12	39.5	125	1.38
13	40.3	122	2.57
14	41.13	134	1.6
15	41.81	137	2.9
16	43.45	147	1.88
17	44.4	153	3.7
18	44.6	154	3.6
19	45.25	158	2.5
20	46.1	164	1.58
21	48.4	180	1.3

for the fact that chlorine is being incorporated without any loss of unsaturation and at the same time without evolution of a corresponding amount of hydrogen chloride, one has to consider alternative ways in which this may be accomplished. This incorporation of chlorine may result from any of the following causes (1) depolymerization, (2) decyclization, and (3) restabilization of the radical adduct by elimination of a hydrogen atom, with double bond shift. It is likely that depolymerization has taken place to some extent, judging by the fact that the phenyl iododichloride product of 50 per cent chlorine content is extremely soluble, whereas a product of similar chlorine content obtained by the action of gaseous chlorine is comparatively insoluble. As regards decyclization, apart from unsaturation measurements, there is no independent method of checking its occurrence, even if it is likely. Lastly, one may consider the postulate of Farmer⁸ regarding the reaction of a radical on unsymmetrically substituted ethylene. According to him, one of the ways that the radical adduct could stabilize itself is by the loss of a hydrogen atom from the carbon atom next to the double bond, resulting in a shift of the double bond. Thus, in the present case the chlorine radicals could possibly attack unreacted isoprenic units (in partially chlorinated rubber) in the manner suggested below.



This may explain the final stage of chlorination with phenyl iododichloride of both deproteinized rubber and pale crepe rubber. The few cases in which the hydrogen chloride evolution is between 5 to 9 per cent is probably brought about by some conditions favoring more substitution reaction.

The further chlorination of pale crepe rubber product of 50.6 per cent chlorine content with gaseous chlorine follows a purely substitutive reaction, as revealed by the copious evolution of hydrogen chloride.

Curve B, Figure 1 (Table 2) shows the change of unsaturation of deproteinized rubber on chlorination with phenyl iododichloride. The main difference from the pale crepe rubber reaction (curve A) is in the very early stage, i.e., up to the incorporation of 36 chlorine atoms per 100 isoprenic units. The introduction of the first 17 chlorine atoms per 100 isoprenic units causes a loss of five double bonds, indicating that additive reaction of chlorine is taking place from the very beginning with a small amount of substitution (0.86 per cent HCl on the weight of rubber). The introduction of the next 18 chlorine atoms causes a loss of 20 double bonds. This can occur only if there is cyclization. Since, during this stage, the hydrogen chloride evolved is less than 1 per cent on the weight of rubber reacting, it is possible that cyclization takes place according to Equations 7, 8 and 9. Thus it is seen that, whereas with pale crepe

rubber, the cyclization reaction seems to occur from the beginning, it occurs with deproteinized rubber only after about 17 chlorine atoms per 100 isoprenic units are introduced. The absence of cyclic structures in a product containing less than about 12 chlorine atoms per 100 isoprenic units has been inferred from an examination of the infrared absorption spectra of such a product. Infrared absorption ascribable to cyclic structures were observed⁹ only in products containing about 25 or more chlorine atoms per 100 isoprenic units.

The ozonolysis studies further show the existence of residual unsaturation in the final products of chlorination. A similar result was obtained by Salomon, van der Schee, Ketelaar, and van Eyk¹⁰ in the radical-catalyzed chlorination of rubber by sulfuryl chloride. Their results arrived at from infrared absorption spectra measurements are of the same order as our results from ozonolysis of the phenyl iododichloride products, as shown in Table 5.

HYDROGEN CHLORIDE EVOLUTION (TABLES 3 AND 4)

The determination of hydrogen chloride evolved during the reaction of phenyl iododichloride with pale crepe or deproteinized rubber confirms that chlorine radicals attack the double bond in preference to attacking the ethylenic

TABLE 5

Reaction product of rubber +80%Cl ₂ (Salomon)		Reaction product of crepe rubber and phenyl iododichloride		Reaction product of deproteinized rubber and phenyl iododichloride	
Chlorine (per cent)	Per cent residual double bonds	Chlorine (per cent)	Per cent residual double bonds	Chlorine (per cent)	Per cent residual double bonds
38.0	42.0	38.0	27.0	38.0	27
44.0	25.0	44.0	21.0	44.0	17
47.0	15.0	47.0	19.0	47.0	17

hydrogen to produce hydrogen chloride. The maximum amount of hydrogen chloride evolved is about 3.6 per cent, except in a few experiments, on the weight of rubber reacting, an observation which is in agreement with that of Bloomfield⁹ with oxygen-free rubber hydrocarbon. A large hydrogen chloride evolution (5 to 9 per cent) during the final stages of chlorination, observed in a few cases, may arise from certain unknown conditions of the experiments favoring a more substitutive reaction of chlorine. The hydrogen chloride evolved is less than 1 per cent in the early stages of the reaction (up to the introduction of 35 chlorine atoms per 100 isoprenic units) and about 2 per cent during the latter stages. The evolution of hydrogen chloride shows that, to some extent, substitutive reaction of chlorine takes place, especially during the final stages. However, one cannot overlook the possibility of the reaction $H + Cl \rightarrow HCl$ as an alternative source for hydrogen chloride evolution.

CONCLUSIONS

1. The reaction between the chlorine liberated by the thermal decomposition of phenyl iododichloride and pale crepe rubber and deproteinized rubber in carbon tetrachloride proceeds mainly by an additive reaction, as revealed by the decrease in unsaturation with chlorination.

2. Cyclization also takes place during the above reaction.

3. The nonrubber components in rubber do not alter the overall reaction between phenyl iododichloride and rubber. However, in the very early stages they have a directive effect in bringing about a cyclization reaction.

4. Since experiments both in an atmosphere of nitrogen and under atmospheric conditions lead to the same overall reaction, it is concluded that atmospheric oxygen has a negligible effect on the reaction.

5. Substitutive reaction of chlorine probably takes place to a small extent, especially during the latter stages of the reaction.

SUMMARY

The loss of unsaturation attending the chlorination of carbon tetrachloride solutions of unmasticated pale crepe and deproteinized rubbers by means of phenyl iododichloride was followed by quantitative ozonization of the chlorinated products, ranging in chlorine contents from 2.3 to 73.6 per cent. It is concluded from such studies that the reaction proceeds mainly by the additive reaction of the chlorine radicals produced by the thermal decomposition of phenyl iododichloride.

The hydrogen chloride found in the preparation of these chlorinated products was determined. It has a value below 1 per cent up to about 15 per cent chlorine content and thereafter it increases. However, this value generally does not exceed 4 per cent. This indicates the occurrence of only a slight amount of substitutive reaction by chlorine.

Cyclization also takes place, probably following an additive reaction of the chlorine radicals.

The main difference between the deproteinized rubber and pale crepe rubber reactions is confined to the very early stages, wherein the nonrubber components have a directive influence in bringing about a slightly earlier onset of cyclization. It is also concluded that atmospheric oxygen has a negligible effect on the reaction.

ACKNOWLEDGMENT

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ENERGY CONSUMED IN THE PLASTICIZATION OF RUBBER ON A ROLL MILL *

EUGENE STALINSKY

When a given weight of natural rubber is plasticized on a roll mill having a speed of its front roll of n turns per minute, the plasticity p of the rubber, measured by a Williams plastometer, and the time t of milling are related in the following way¹:

$$p = \frac{K}{\sqrt{nt}} + p_0 \quad \text{or} \quad p = \frac{K}{\sqrt{N}} + p_0 \quad (1)$$

In these two equations, N represents the total number of turns of the front roll of the mill to carry the rubber to a plasticity p ; p_0 represents the plasticity of the rubber reached at a high value of N , and K is a constant.

The factors p_0 and K depend on the weight of rubber plasticized and on the temperature at which plasticization is effected.

It will now be shown that there is a linear relation between the power P (in kilowatts) expended by the mill at a given moment and the corresponding plasticity of the rubber:

$$P = K_n \cdot p \quad (2)$$

This relation has been verified by the experimental results obtained by Haehl and Le Bras² in plasticization tests carried out at 60° C with 350 grams of first-latex rubber whose initial plasticity was 4.31. The authors utilized a Troester laboratory mill, the speed of whose rolls could be adjusted at any point in the range of 12–36 turns per minute.

In Table 1, the values of the power P and the plasticity p as a function of the time t in minutes, as found by Haehl and Le Bras for roll speeds of 12 and 18 turns of the front roll per minute, are shown.

From the data in Table 1, we have calculated the values of the ratio, $P/p = K_n$, as well as the values of the factors p_0 and K in Equation (1). They were found to be: $p_0 = 1.6$, and $K = 13.7$.

Actually it was found that, for each of the roll speeds considered, the values of P/p are practically constant. The mean values of K_n as a function of the roll speed are, as shown in Table 1, 1 and 1.10 for speeds of 12 and 18, respectively, turns per minute.

In the same way, we have found that $K_n = 1.80$ for a roll speed n of 36 turns per minute.

The curve representing K_n as a function of n is practically a straight line, and is expressed by the equation: $K_n = 0.034 n + 0.58$.

The ratio P/p is a linear function of the speed of the front roll.

Equations (1) and (2) make it possible to calculate the total energy consumed in milling the batch of rubber to plasticity p . Let us assume that P is the power and p is the plasticity measured at instant t , and that they are

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TABLE 1

Time (min.)	n = 12t/min.				n = 18t/min.			
	N	p	P _{kw}	P/p	N	p	P _{kw}	P/p
10	120	2.85	2.7	0.95	180	2.65	2.8	1.06
20	240	2.51	2.5	1.00	360	2.35	2.7	1.16
30	360	2.25	2.4	0.94	540	2.13	2.5	1.17
40	480	2.11	2.2	1.04	720	2.07	2.3	1.11
50	600	2.07	2.1	1.01	900	2.03	2.2	1.08
60	720	2.01	1.9	1.06	1080	2.00	2.1	1.05
	Average 1.00				Average 1.10			

constant during a time interval dt . The work dP done is represented by the relation: $dP = Pdt = K_n \cdot p \cdot dt$.

By replacing p by the value derived from Equation (1), the following relation is obtained:

$$dT = K_n \left(\frac{K}{nt} + p_0 \right) dt$$

which, by integration from 0 to t becomes:

$$T = K_n \int_0^t \left(\frac{K}{\sqrt{n} \cdot \sqrt{t}} + p_0 \right) dt = K_n \left(\frac{2K\sqrt{t}}{\sqrt{n}} + p_0 \cdot t \right) \quad (3)$$

Haehl and Le Bras found experimentally that the energy consumed during the plasticization of 350 grams of first-latex rubber on a laboratory roll mill at 60° C and with a roll speed of 18 turns per minute, from an initial plasticity of 4.31 to a plasticity of 2.5 was 0.82. The value calculated from Equation (3) is 0.77, which would appear to be reasonably close to the experimental value of 0.82.

Equation (3) includes two terms. The first of these, $2K_n(K\sqrt{t}/\sqrt{n})$, represents the power consumed by the actual operation of plasticization itself. The second term, $K_n \cdot p_0 \cdot t$, represents, from the practical standpoint, the power consumed when the mill runs empty, for the plasticity value p_0 represents a final state of the rubber when it is so soft that it offers no resistance to milling.

In conclusion, Equation (3) makes it possible to determine the total power consumed in milling rubber to a given state of plasticity. In addition, it indicates the power consumed by the actual plasticization itself and makes possible a comparison of different types of rubber independent of the power consumed when the particular mill runs without any load.

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A SIMPLE OBJECTIVE METHOD FOR ESTIMATING LOW CONCENTRATIONS OF OZONE IN AIR *

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Cracking of rubber, subject to strain, both natural and synthetic, by atmospheric ozone has become a major problem in the increasing usage of rubber in services for which its physical properties so admirably suit it. The cracks, which may vary widely in size, make the article unsightly and finally unserviceable. Rubber goods have been found to suffer from rapid deterioration in urban areas where recent studies have shown high ozone concentrations.

The desirability of determining the atmospheric ozone concentration under various conditions has been pointed out by Reynolds¹, van Rossem and Talen², Crabtree and Erickson³, and Bradley and Haagen-Smit⁴. They suggest the use of a standard rubber compound as a means of accomplishing this objective, on the presumption that the cracking of rubber subjected to strain is a specific test for the presence of ozone.

The Crabtree and Erickson procedure involves stretching a specimen of the standard compound (which is cured in a polished mold and has its glossy surface preserved by applying a sheet of cellophane over it until ready for use), exposing to the atmosphere to be tested, and observing with a magnifying glass (7-8 power) at five-minute intervals for the appearance of minute pin-point eruptions. The first appearance of these eruptions constitute the end point of the test.

The Bradley and Haagen-Smit method consists of exposing a doubled $\frac{1}{16}$ -inch strip, also cured in a polished mold, to a stream of air to be tested at some constant rate of flow. The end point is the moment when cracking is first observed under a magnifying glass (4-power).

Both methods depend to a considerable degree on the judgment and visual acuity of the observer. In this laboratory, attempts were made to evaluate the Crabtree and Erickson procedure by comparing the ability of different observers to discern the presence or absence of the pin-point eruptions. The lack of agreement was so serious as to cast considerable doubt on the value of the procedure for general use.

Various schemes were considered in an attempt to utilize rubber as the "reagent" in a manner which would be objective and would not depend on the judgment of the observer. In addition, it was desired that the test be as simple and rapid as possible and not require any services such as electric or chemical supplies, so that it could be used in locations where these services would not be available.

Creep in tension at constant stress is a sensitive means of measuring the damage caused by ozone cracking. The cracks reduce the cross-sectional area of the specimen, thereby increasing the strain. The values for creep obtained in this manner would, however, also include ordinary creep. One means of differentiating between the two types of creep is to test two specimens simul-

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taneously, one subjected to air and ozone and the other protected from ozone, but in the presence of atmospheric oxygen. The difference between the values of strain as a function of time would be due to ozone cracking. Protection of a strand of rubber from ozone is easily accomplished, since ozone diffuses very slowly and is readily decomposed by cellulose materials. Protection may be accomplished by a narrow tube or enclosure, lined with ordinary blotting paper,

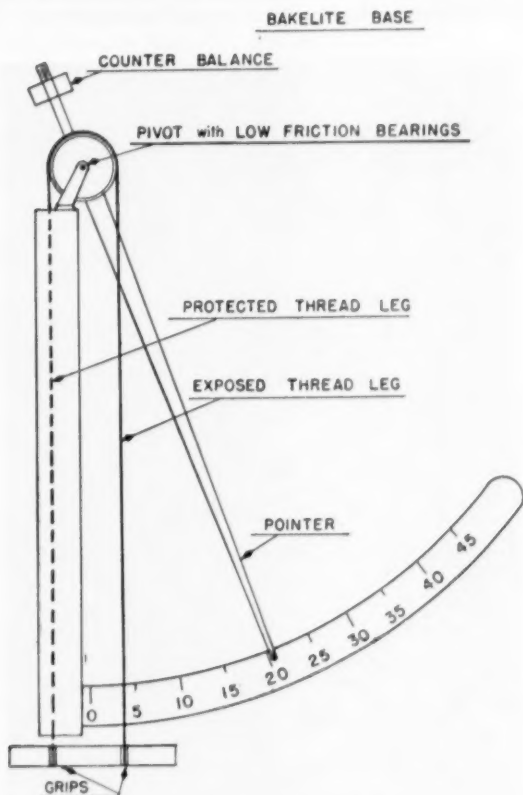


FIG. 1.—Schematic diagram of B. F. Goodrich Ozonometer.

open at the ends so that oxidation or other effects, if they occur, will be equivalent in both strands.

DESCRIPTION OF THE INSTRUMENT

To utilize the principle for measuring ozone attack discussed above, an instrument called the Ozonometer has been constructed. A diagram of the instrument is shown in Figure 1 and a photograph in Figure 2. It consists essentially of a low friction bearing pulley which maintains the stress equalized between the two legs of the single stretched rubber thread, one leg of which is

subject to ozone attack, and one protected from ozone as described above. At the start of the test, the stress in each leg is equal and remains so throughout, owing to the rotation of the pulley effecting a balance. The strain, however, varies from the initial elongation, i.e., 97 per cent of the original strain in the protected leg and 103 per cent in the exposed leg at the maximum rotation of 45 degrees. This action, then, is creep under conditions of equal, but decreasing stress in the two legs of the rubber thread. Since the stress is identical in both legs, the difference in the amount of creep is proportional to the reduction

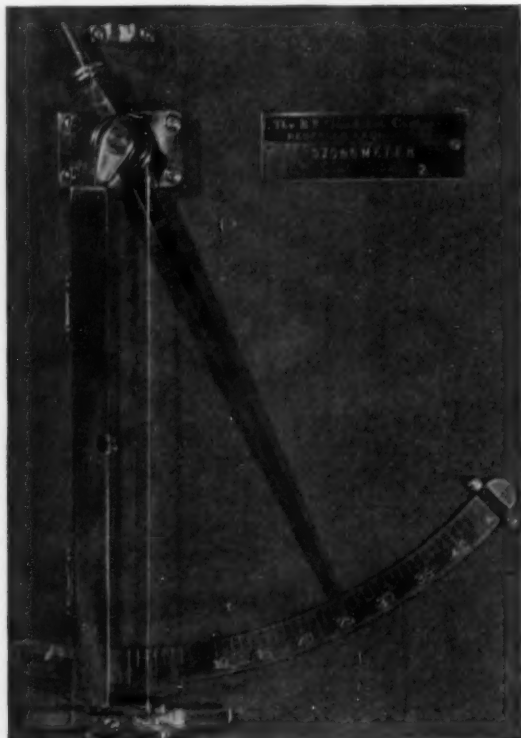


FIG. 2.—Photo of B. F. Goodrich Ozonometer.

of cross-sectional area of the exposed leg. Cracking at the ends of the protecting enclosure is cancelled by that of the exposed leg. The effects of oxygen-induced creep and thread non-uniformity for all practical purposes are cancelled out by this arrangement.

The test-specimen selected as the standard was a length of natural-rubber golf-ball thread, 0.075 inch wide and 0.015 inch thick. This thread is readily available, is manufactured in a suitable form, and is uniform in modulus and dimensions. The bulk of the experimental work was done with 100 per cent elongation of the thread.

TEST PROCEDURE

Directions for operating the instrument are as follows:

- (1) Load the test-strip of the proper length by clamping an end in each grip and stretching the strip over the pulley.
- (2) Adjust the position of the pointer to the vicinity of the zero point.
- (3) Deflect the pointer to the maximum deflection and allow it to swing freely to its balanced position to equalize the strain around the pulley.
- (4) Close the protective door over one leg.
- (5) Place in atmosphere to be tested (entire instrument must be at temperature equilibrium with surroundings).

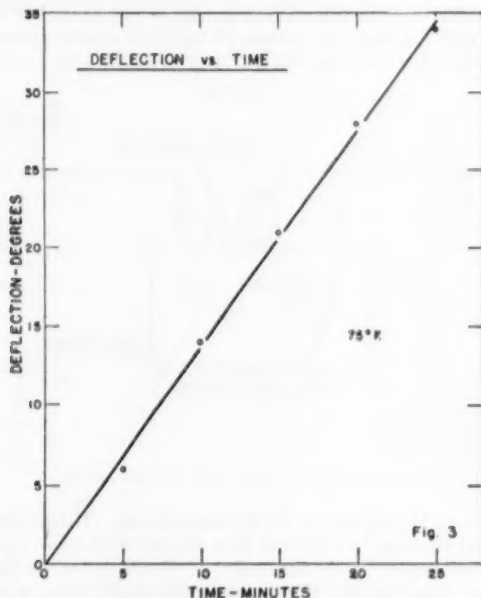


FIG. 3.—Angular deflection vs. time for the Ozonometer.

- (6) Vibrate the base lightly to overcome any bearing friction.
- (7) Read the deflection indicated.
- (8) Repeat steps (6) and (7) at intervals of five minutes more or less, depending on the rate of ozone attack. Twenty to 30 minutes' test time is sufficient for most purposes.
- (9) Plot the best fitting straight line for the deflection vs. time curve.

A typical curve for angular deflection vs. time is shown in Figure 3, obtained for a specific ozone concentration. The curves obtained are essentially straight lines for the times considered, so that the slope of the curve, or degrees of deflection per minute, may be used as an indication of the severity of ozone attack.

CALIBRATION EQUIPMENT

In order to investigate the variables that affect the operation of the Ozonometer, the equipment shown in Figure 4 was constructed. It was also found useful in studying compounding variables at constant ozone concentrations. Laboratory compressed air, which was found to contain no ozone, was used to provide an ozone-free source of air for test purposes. It was ozonized to the desired extent by a generator consisting of four Westinghouse 794H Sterilamps. Each lamp operates in series with a 40-watt incandescent lamp to provide the required voltage. The ozone lamps were enclosed in a glass cylinder through which a measured volume of air was passed. By varying the number of lamps in operation and (or) the rate of air flow, the ozone output can be controlled. This generator gave a steady supply of ozonized air.

The test chamber used in this work was a glass jar, 18 inches in diameter by 12 inches high, with a ground top edge. The lid was plate glass and had the ozone inlet and outlet as well as the stirring facilities attached to it. A seal

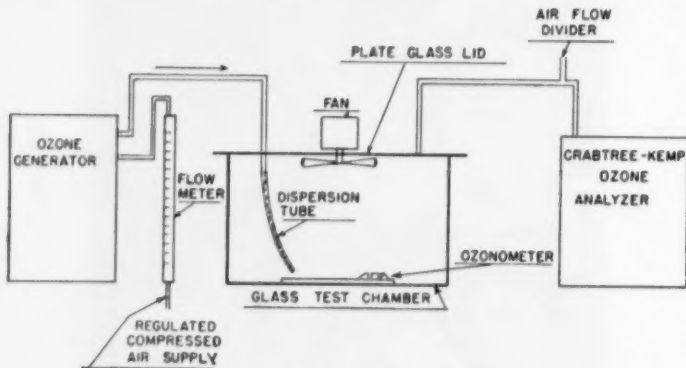


FIG. 4.—Calibration equipment for the Ozonometer.

was effected between it and the jar by silicone grease. It was found necessary to use mechanical stirring in addition to a simple dispersion tube to prevent stratification, as evidenced by smoke tests and Ozonometer readings. In addition, tests showed that besides the fan and dispersion tube a minimum flow rate of one cubic meter per hour of the ozonized air for this volume chamber was required to secure the same reaction on the Ozonometer, as was found outdoors or in a good sized room indoors where convection currents and wind provide the circulation.

EFFECTS OF TEST VARIABLES

The calibration, determined by use of the equipment described above with the standard golf ball thread, is shown in Figure 5. It is seen that the rate of deflection is a direct function of ozone concentration, determined by the chemical method described by Crabtree and Kemp.⁵ The effect of temperature agrees with the data of other investigations⁶ in that the severity of ozone attack increases directly with temperature.

To confirm that the reaction was due to ozone alone, tests were made in atmospheres of tank oxygen, lamp-grade nitrogen, or laboratory compressed air

in the glass chamber. Since no deflections with the Ozonometer were observed in any of these cases, it was assumed that the angular deflection noted in ordinary and ozonized atmospheres was due to ozone. Another investigator² also confirmed these results for chlorine, nitrogen oxides, and sulfur dioxide in that no cracks were formed.

It was theorized that the effect of creep on the two legs of the specimen effectively cancels out. To check this, tests were made with both legs exposed to various atmospheres. No angular deflection of the pointer was noted, even though those containing ozone caused cracks in both legs of the specimen.

The effect of varying the thread elongation is shown in Figure 6. The maximum rate of deflection is at approximately 100 per cent elongation for this particular rubber thread material. Higher modulus stocks have the maximum

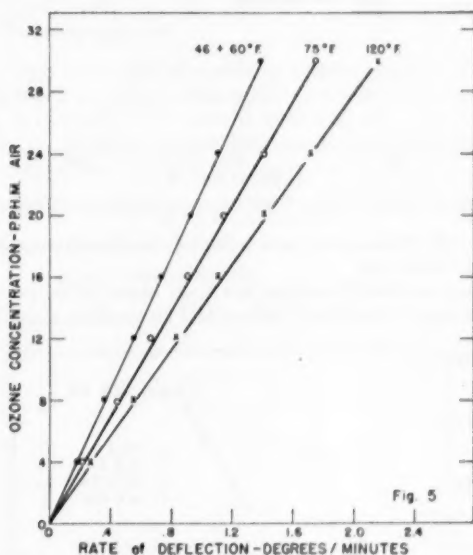


Fig. 5.—Ozonometer calibration results at different temperatures.

reaction at lower elongations. Ozone cracking studies have established that low elongations give large destructive cracks, but few in number; while high elongations give more numerous, but smaller cracks. Evidently the greatest reduction in cross-sectional area is found at an intermediate elongation, which for this low modulus material (golf-ball thread) is about 100 per cent. Other compounds of rubber vary in this reaction, depending on their modulus.

It is possible that crystallization of the rubber sample limits the range of operating temperature in use of this instrument as an ozone concentration measuring device, since cooled and strained rubbers crystallize rapidly⁷. For the same reason, elongations above 100 per cent probably should be avoided in tests at room temperature.

The effect of humidity on the rate of deflection is shown in Figure 7. The rates of deflection were identical for relative humidities of 0, 10, and 46 per cent,

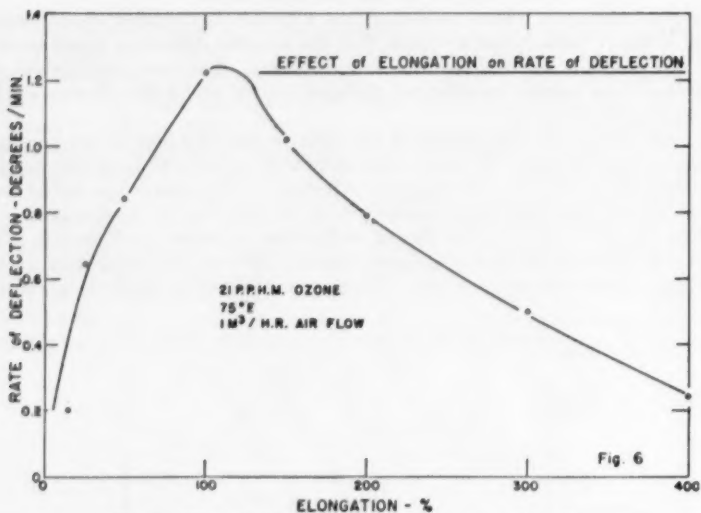


FIG. 6.—Effect of rubber-thread elongation on rate of deflection.

Relative humidity of 100 per cent gave a slightly increased rate of deflection for a given ozone concentration.

In many instances direct sunlight has been observed to prevent the gross cracking due to ozone of stretched rubber and to produce a shallowly checked

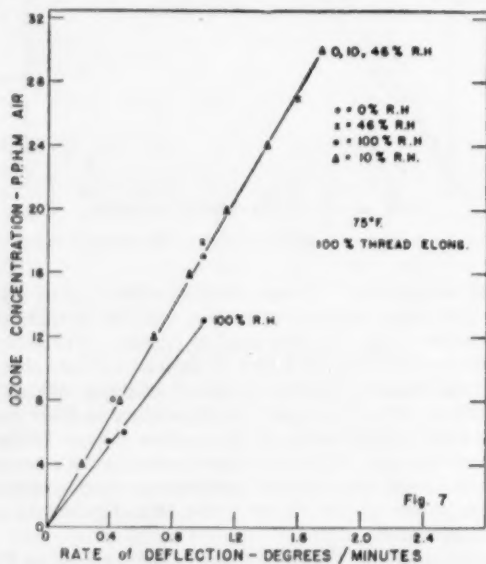


FIG. 7.—Effect of relative humidity on rate of deflection.

TABLE 1
OZONOMETER CALIBRATION SUNLIGHT AND SHADE

November 8, 1953—Weather Clear

Test no.	Machine no.	Sunlight			Shade		
		Deflection in 30°-degrees	Temp. (° C)	O ₃ Concn. pphm.	Deflection in 30°-degrees	Temp. (° C)	O ₃ Concn. pphm.
1	2	18.4	14	13	14.4	10	11
2	2	24.4	16	15	17.0	11	13
3	1	23.0	18	13	12.2	13	9
4	1	16.2	22	9	15.0	14	11
5	2	14.1	21	8	11.4	15	8
6	2	18.0	21	10	9.7	15	8
7	1	21.0	21	12	15.6	15	11
8	1	14.0	25	8	13.0	15	10

Av. O₃ concentration, 11 pphm.

10 pphm.

surface which, after the onset of checking, deteriorated slowly. From these observations, it was a matter of some conjecture whether Ozonometer readings could be made in sunlight. The results obtained with the Ozonometer, however, were identical as to ozone concentration when the temperatures of the test strips were taken into consideration, as shown in Table 1. Measurements

FIG. 8.—Ozone concentration vs. air flow rate; ozone measured by ozonometer and by chemical means.

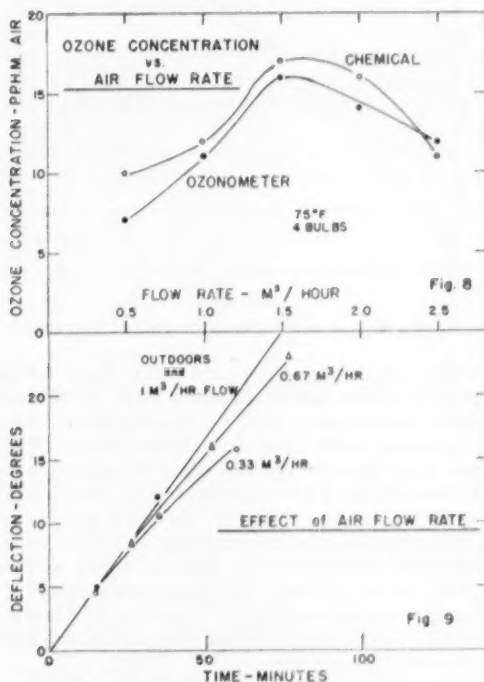


FIG. 9.—Effect of air flow rate on deflection.

were made simultaneously with two machines side by side, one shaded, and the other in bright sunlight. These results are in agreement with those of a recent study⁴.

In outdoor tests, the wind varies both in direction and velocity, with direction having no appreciable effect. To determine the effect of air velocity on the Ozonometer, tests were made in the calibration chamber. Increasing the rate of flow of air through the calibration chamber approximates the effect of an increase in wind velocity.

In Figure 8 ozone concentrations measured by means of both the Ozonometer and chemical methods are plotted as a function of the rate of the ozonized air through the test chamber. Flow rates of one cubic meter per hour and above gave essentially equal results by both methods of measurement, but, below one cubic meter per hour flow rate, the Ozonometer readings were low,

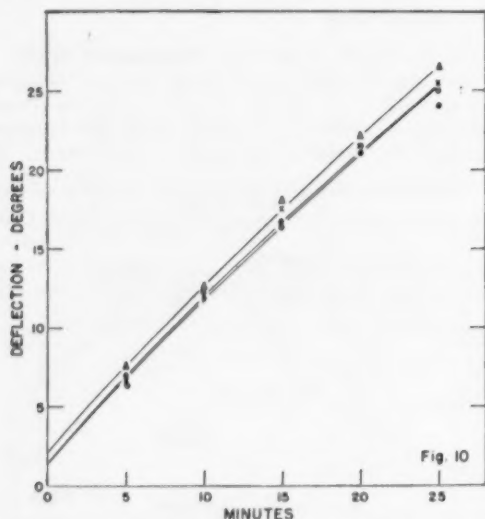


Fig. 10.—Reproducibility of deflection results for a given lot of rubber thread.

when compared with chemical measurements. The shape of the two curves is due to the variation of ozone output resulting from the increased flow rate. Up to flow rates of 1.5 cubic meters per hour the efficiency of ozone production of the generator increases faster than the dilution effect. Flow rates above 1.5 cubic meter per hour show the dilution effect to predominate.

Results of outdoor tests using two Ozonometers are shown in Figure 9. One instrument was in the calibration chamber; the other nearby in the open air. Air was pumped through the calibration chamber at various rates, as shown on the graph. The deflections measured as a function of time showed that at flow rates below one cubic meter per hour the Ozonometer gave low deflection *vs.* time curves compared to measurements in the open air. However, a flow rate of one cubic meter per hour through the calibration chamber produced identical deflections with those of the open air.

Tests in laboratory room air showed essentially the effect noted in the out-

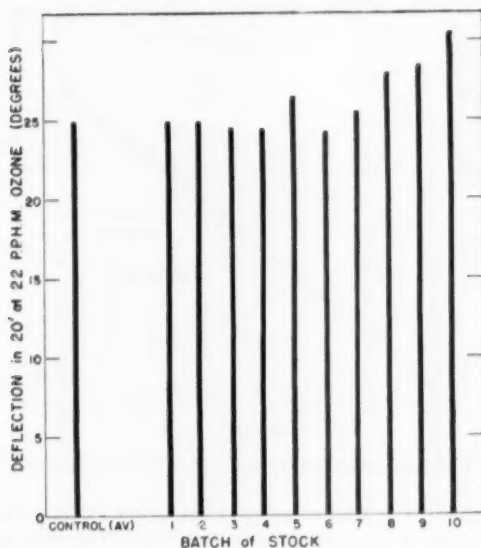


FIG. 11.—Batch to batch rubber thread variation effect on deflection.

door tests. The convection currents within the room gave adequate circulation, so that measurements in the room air agreed exactly with those made in the calibration chamber with one cubic meter per hour of the room air passing through it.

These tests were made to determine the effect of air velocity on the operation of the Ozonometer as an ozone measuring device, compared to chemical

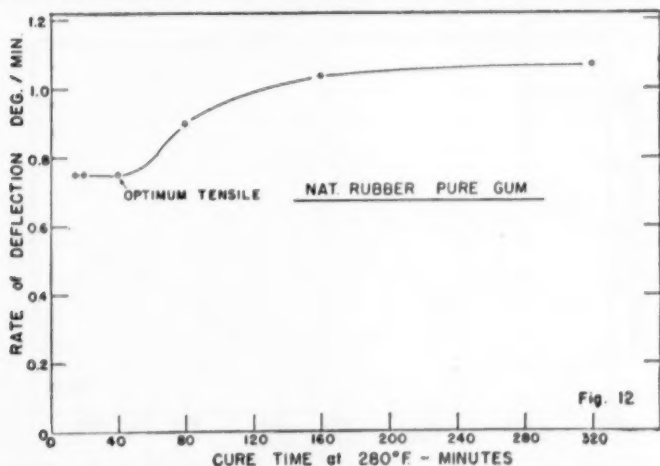


FIG. 12.—Effect of cure time of rubber thread on deflection rate.

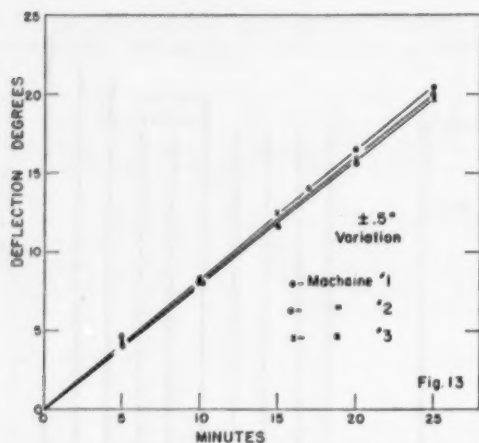


FIG. 13.—Reproducibility of deflection data with three machines.

methods of analysis. The results indicate that wind velocity has no effect on Ozonometer measurements of ozone concentration. The data also show that low readings with the Ozonometer are probably due to poor dispersion of ozone in a closed chamber or stratification of the ozone in the atmosphere of the chamber.

The reproducibility of data for a given lot of thread is shown in Figure 10. Figure 11 shows results for 10 lots of thread taken at random from production. Seven of the 10 lots agree quite well; while three deviate somewhat more than is desirable. This deviation may be due to the state of cure.

Figure 12 shows the effect of cure time on the rate of deflection for a stock similar to the control. The rate of deflection is essentially constant until over-

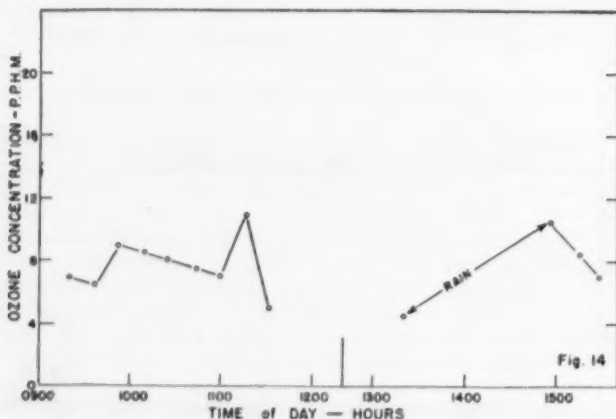


FIG. 14.—Outdoor ozone concentration at Brecksville, Ohio, for one day, measured by Ozonometer.

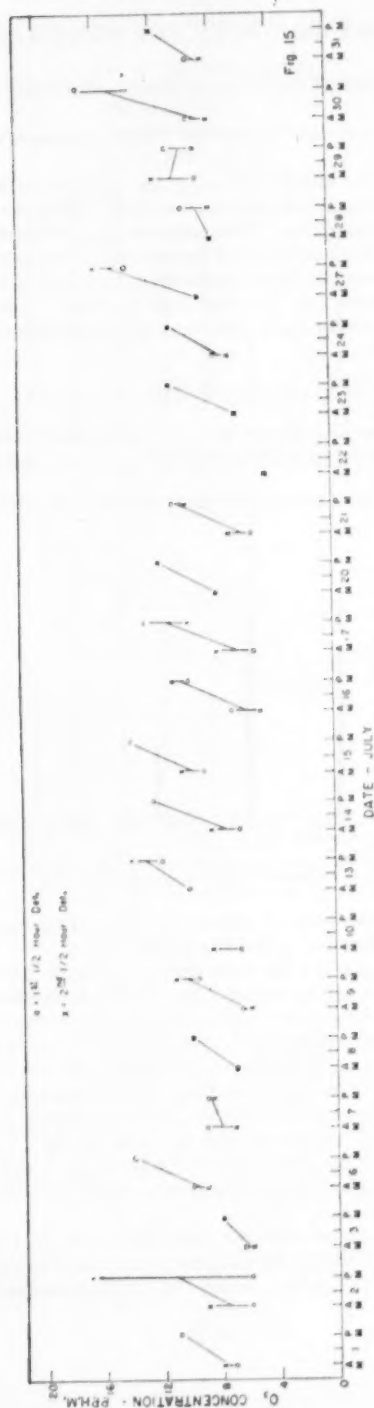


FIG. 15.—Outdoor ozone concentration at Brecksville, Ohio, July, 1954, measured by the Ozonometer.

cure, whereupon the rate of deflection increases, indicating more severe ozone attack.

The reproducibility of data among the three instruments of this laboratory is shown in Figure 13.

If the data for thread rubber and machine reproducibility are used in conjunction with the results of the chemical analysis and rate of deflection study, some idea of the correspondence of the determinations with the Ozonometer and those of the chemical method may be ascertained. From these data it would appear that the Ozonometer determinations correspond with, and are as consistent as, measurements by the chemical method. The accuracy of the chemical method is reported to be ± 5 per cent⁵ at ozone concentrations of 3 to 25 pphm. of ozone in air.

APPLICATIONS OF THIS MACHINE

There are two general types of use for which the Ozonometer is ideally suited. They are measuring ozone concentrations, and determining the resist-

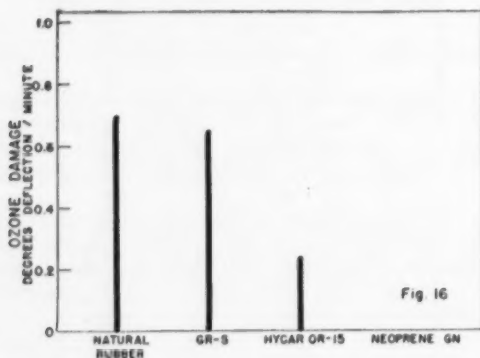


Fig. 16.—Comparison of rubber polymers at fixed ozone concentration by means of the Ozonometer.

ance to ozone attack on strips of rubber compounds of various formulations under controlled conditions of ozone concentration.

Typical of the first use are the data shown in Figure 14, where ozone concentrations were measured just outside the Goodrich Research Center. Such data are of interest because they relate ozone concentration with the time of day and meteorological conditions. Morning and afternoon determinations of the ozone concentration outside the laboratory for the month of July are shown in Figure 15. The morning readings were taken at 8:30–9:30 a.m.; the afternoon readings were at 3:15–4:15 p.m. Concentrations, in general, were found to be higher in the afternoon than in the morning. The range of ozone concentrations in this study was from 4 to 16 parts per hundred million of air, which is considerably higher than has been reported in any location except near Los Angeles.

Typical of the second use are the data illustrated in Figures 16 and 17. Figure 16 summarizes the data for gum recipes of various polymers compared as to ozone resistance at 25 pphm., using 100 per cent elongation of the rubber strip.

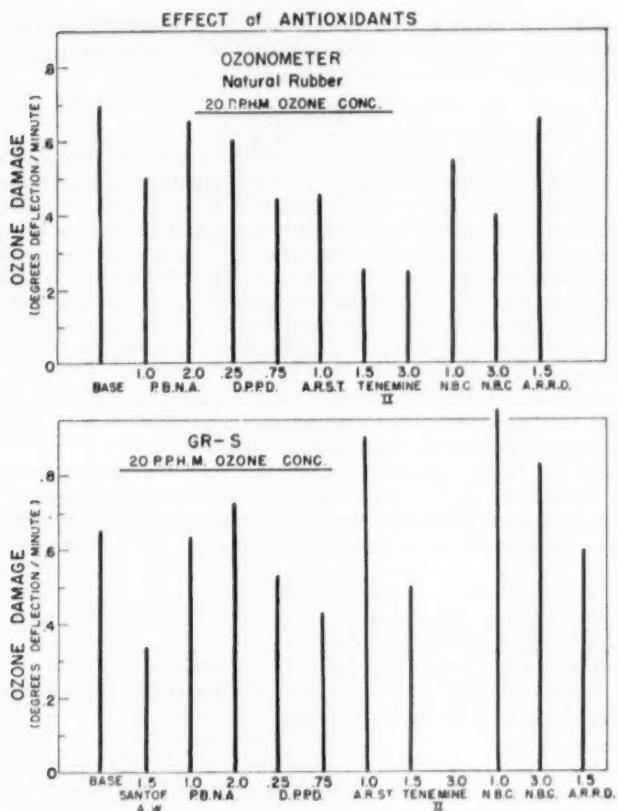


Fig. 17.—Comparison of effectiveness of various antioxidants in natural rubber and GR-S in preventing ozone damage.

TABLE 2

Natural Rubber		GR-S	
Blended smoked sheet	100	L. T. polymer	100
Stearic acid	1	Zinc oxide	5
Zinc oxide	5	Tetramethylthiuram	
Altax*	1	disulfide	4
Sulfur	2.5	Antioxidant variable	
Antioxidant variable			
Abbreviation		Antioxidant	
P.B.N.A.		Phenyl-2-naphthylamine	
D.P.P.D.		Diphenyl- <i>p</i> -phenylenediamine	
N.B.C.		Nickel dibutyldithiocarbamate	
A.R.R.D.		AgeRite Resin D†	
A.R.ST.		AgeRite Stalite†	
SANTOF. A.W.		Santoflex AW‡	

* 2-2' Benzothiazyl disulfide.

† R. T. Vanderbilt Co., New York, N. Y.

‡ Monsanto Chemical Co., St. Louis, Mo.

Figure 17 illustrates typical results for various antioxidants in natural rubber and GR-S. The base recipes are shown in Table 2, with an explanation of the abbreviations for the antioxidants used in Figure 17.

SUMMARY

A simple, accurate, and objective method for the estimation of ozone concentrations in air has been developed. It is based on the well known reaction of ozone on rubber subjected to strain, namely, the formation of cracks. The differential creep of a natural rubber thread, one-half of which is subjected to the ozone-containing atmosphere, the other half protected from ozone, is a sensitive measure of the severity of ozone attack or cracking. This differential creep or deflection is essentially linear with time at a given ozone concentration, and the rate of deflection is directly proportional to the ozone concentration. The variables of specimen, machine, temperature, thread elongation, humidity, and sunlight were investigated.

The instrument, the B. F. Goodrich Ozonometer, is a small, self-contained unit, which may be operated in the horizontal or vertical position. Two areas of usefulness for this method and machine exist.

1. Tests for ozone concentration in locations inaccessible to ordinary chemical methods by virtue of the equipment and services required.

2. Comparisons of the resistance of rubber compounds to ozone attack under conditions of controlled ozone concentration.

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ELECTRON MICROSCOPIC STUDY OF THE LOCUS OF LATEX REACTION *

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The outstanding example of the study of reaction loci in an emulsion system is Harkins's work¹ in the field of emulsion polymerization. A simpler case presents itself for study when chemical reactions are carried out with preformed polymer emulsions (latexes), as in the hydrochlorination of polyisoprene latex². Here the reaction consists in the progressive conversion of the individual unsaturated isoprene units to their hydrochlorinated form:



the polymer particles preserving their identity throughout the reaction. The hydrochloric acid arrives at the site of reaction by a series of diffusion processes from the vapor phase and through the continuous aqueous phase. In principle there are still two loci at which the isoprene units may react with this reagent: in the bulk of the particle and at (or near) the interphase between the aqueous acid and the polymer particle. We were led by kinetic experiments³ to conclude that the two loci do react at different rates and by different mechanisms, and it is the purpose of this report to provide quantitative evidence for this conclusion. At the same time we wish to put on record some observations connected with the electron microscopic technique used in the investigation.

The situation in the latex hydrochlorination reaction bears some resemblance to that in Smith's work⁴ on emulsion polymerization seeded with preformed polymer particles. This proved that the polymerization took place in the preformed particles, after the relevant reagent, viz., the monomer, had arrived there by diffusion. However, no distinction has arisen in emulsion polymerization between the bulk locus and the surface locus of a particle of polymer. The technological importance of this new distinction in rubber chemistry is stressed below.

Our kinetic observations³ suggested that a fast conversion of isoprene units near the polymer particle surface is responsible for observed abnormalities near the beginning of the rate curves. This is quantitatively confirmed by correlating the extent of the initial "jump" in the rate curves, measured by the intercepts *P* (Figure 1), with measurements of the specific surface of the particles by means of electron micrographs (Figures 2–4). Details of the preparation of the latexes and of the kinetics and mechanism of the hydrochlorination in the bulk of the polymer particles, whose rate is measured by the slope of the straight lines in Figure 1 have been published³. The lines refer to natural (Hevea) latex and two synthetic polyisoprene latexes. Two further synthetic latexes are reported in Table I, and the total range of average particle diameters studied

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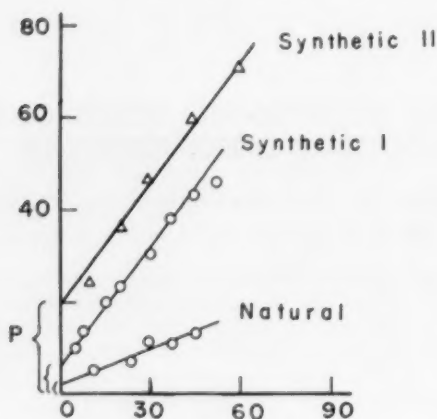


FIG. 1.—Rate curves for the hydrochlorination of polyisoprene latexes at 300° abs. and 2 atm. of HCl.

is seen to be tenfold. The correct method of averaging n particles of diameters D_i so as to obtain a measure of the specific surface of a given latex, and thus of its total locus for the surface reaction, is to calculate the surface average diameter D defined thus:

$$\pi D^3 = \left(\sum_i \pi D_i^3 \right) / n$$

i.e.,

$$D = \left[\left(\sum_i D_i^3 \right) / n \right]^{1/3} \quad [1]$$

The thickness τ of the outer shell of a sphere of diameter D , which comprises $P\%$ of the sphere by volume, may then be computed thus:

$$\tau = D(1 - 0.2155(100 - P)^{1/3})/2 \quad [2]$$

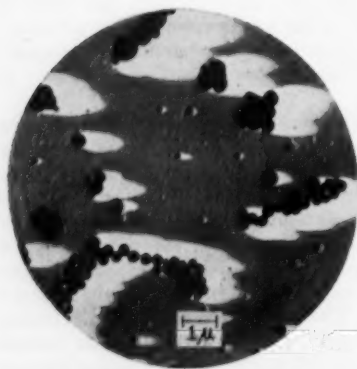


FIG. 2.—Natural-rubber hydrochloride latex.

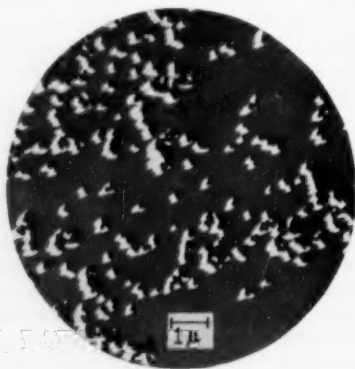


FIG. 3.—Synthetic polyisoprene hydrochloride latex I.

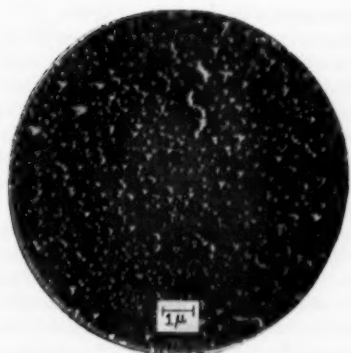


Fig. 4.—Synthetic polyisoprene hydrochloride latex II.

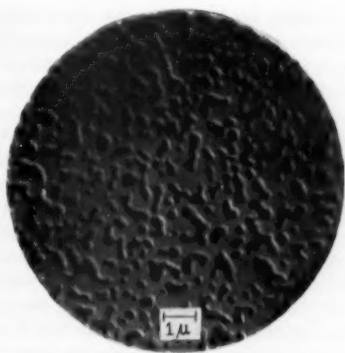


Fig. 5. Synthetic polyisoprene latex I.

All samples shadow-cast at approximate angle $\cot^{-1} 2.5$.

The values of τ found for the one natural and four synthetic latexes in Table I show very satisfactory constancy at 15 ± 2.5 Å. This confirms the kinetic inference that units privileged for fast reaction, react in the vicinity of the particle surface, i.e., the interphase with the aqueous phase. The result can be expressed by saying that the extent of the fast initial hydrochlorination reaction is governed merely by the percentage P of the polymer units which lies within $\tau = 15$ Å. of the particle surfaces. This shows indirectly that the subsequent main reaction, corresponding to the linear rate plots (Figure 1), occurs at the other possible reaction locus, namely, inside the bulk of the polymer particle. The kinetic evidence shows that the rate of the surface reaction, which is here too fast to be measured, must fall off rapidly with the progress of the surface reaction, and once the first four layers have reacted, the surface rate becomes negligible. This may be expressed by saying that the surface reaction has a very high reaction order. With natural rubber the thickness τ increases with temperature at constant HCl pressure. This, and other reasons, suggest that the falling off of the surface reaction is governed by a diffusion rate. If so, the rate of the surface reaction should be sensitive to prior cross-linking of the rubber. This has been investigated in vulcanization studies to be reported⁸.

All latex samples (saturated with HCl in the case of hydrochlorinated samples) were prepared for examination in the electron microscope by diluting with distilled water and then placing a single drop of the dispersion on the standard collodion-covered specimen grids used in electron microscopy. The specimen was then allowed to dry in a desiccator. In some cases the samples were shadow-cast with gold/palladium alloy in order to enhance contrast.

TABLE I
SURFACE HYDROCHLORINATION REACTION (300° ABS., 2 ATM. OF HCl)

$P\%$	D (unshadowed), Å.	D' (shadowed), Å.	τ , Å.	τ' , Å.	Latex
2.0	(4500)	—	15	—	Natural
6.25	1175	1400	12.5	14.7	Synthetic I
15	670	—	15	—	Synthetic III
20	467	700	17	24.9	Synthetic II
21	460	—	17.4	—	Synthetic V

Owing to their narrow size ranges, the synthetic latexes (Figures 3, 4) allowed sufficiently accurate values of the diameter D to be obtained by averaging a few particles chosen at random on the electron micrographs. In natural latex the particles are far from uniform in size (Figure 2), but two different samples were found by van den Tempel⁶ to agree closely in distribution curve and D , so that his value of $D = 4500$ Å. was accepted⁷. All our micrographs were taken at a magnification of $8000\times$. Table I lists separately the surface average particle diameters D measured on non-shadow-cast specimens and those, denoted by D' , measured on shadowed specimens of synthetic latexes I and II. The maximum width of the shadow was taken as D' , and this can be measured with somewhat higher precision than D , because of the higher definition of micrographs of shadowed specimens. The value of D' is seen to be larger than D by about 230 Å. in both cases. The effect of shadow-casting in increasing the apparent particle size has been repeatedly noted by other workers, but its explanation is not quite certain. Kern and Kern⁸, and Cosslett⁹ independently explain the effect in terms of the surface charge of the particle producing the action of an electrostatic lens. The former authors imagine the lens to act on the electron beam in the microscope. A spuriously enlarged picture of the unshadowed particle is thus produced, while the shadowed particle, which allows its surface charge to leak away, gives a correct measure. Cosslett, however, considers the lens to affect the metal atoms in the shadowing process, in which case we must assume that the unshadowed particle gives the correct measure of the diameter. The chemical evidence based on our measurements of the intercepts P (Figure 1) appears to support Cosslett's explanation, inasmuch as the unshadowed diameters D lead via Equation [2] to noticeably more constant values of τ , when compared to the values τ' obtained via the same equation from the shadowed diameters D' (as shown in Table I).

Whatever the explanation of the effect, it is apparent from micrographs shown in Kern and Kern's papers that the effect is relatively more marked with smaller particles (such as bacteriophages). Our measurements confirm this and suggest in fact that:

$$D' - D = 230 \text{ Å} \quad [3]$$

The almost identical difference of 250 Å. between shadowed and unshadowed particles was also observed by Kern and Kern on much larger (polystyrene) latex particles. The suggestion of the simple law of Equation [3] may assist in the final theoretical explanation of the phenomenon.

Comparison of electron micrographs before and after hydrochlorination of our latexes reveals several interesting features (see Figures 3 and 5). The change from the rubbery amorphous to the glassy state (with or without embedded crystalline regions¹⁰) during hydrochlorination is reflected in a change of appearance of shadow-cast samples. Rubbery particles are flattened (Figure 5) and appear disklike rather than spherical, owing to wetting of the collodion support by the deformable particle. The glassy particles are so stiff as not to be visibly flattened, and are thus much more useful for measuring the particle diameters. Although much irreversible aggregation occurs in drying out the rubbery samples, the ultimate particle size before the hydrochlorination reaction is seen to be essentially the same as after the reaction. This confirms that the particles preserve their identity during the reaction without dissolution or coagulation. (The volume change due to the actual reaction can, of course, be accurately computed from density data, but changes the diameter by only a few per cent.) The contrast in the micrographs, particularly in the case of un-

shadowed particles, increases considerably in the course of the reaction, owing to the relatively high scattering power of the chlorine atoms introduced thereby. This suggests the usefulness of reactions like hydrohalogenation or halogenation of latexes, after suitable stabilization against coagulation, when it is desired to study size distributions by electron microscopy.

The demonstration here given of the occurrence of a polymer particle surface reaction locus, controllable by such variables as particle size and temperature, has colloid-chemical and technical importance. That the hydrochlorination reaction is not merely an isolated instance of this effect is suggested by similar rate curve "jumps" in the cyclization of Hevea latex². Preliminary work suggests that, in the vulcanization of latex, a surface locus can also be observed. In this reaction the technical effect would be expected to be particularly marked. For example, a lightly and uniformly cross-linked particle would give a useful prevulcanized latex. If, however, the reaction (interrupted after 1 per cent or so of conversion in practice) were found to be largely concentrated in the surface layer, as the present work shows the hydrochlorination reaction to be at such low conversions, one would obtain what might be described as an unvulcanized particle surrounded by a shell of ebonite, which would be technically useless. Differences in film strength of prevulcanized latexes at constant combined sulfur are thought to be connected with the variability of the contribution of the surface locus from one vulcanization recipe to another.

ACKNOWLEDGMENT

The authors are indebted to Professor P. D. Ritchie for his kind interest in this work.

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- ⁷ Rough estimates from our own micrographs led to somewhat lower values (2500-3000 Å.), while preliminary measurements by Coslett (quoted by Cockbain, *Trans. Inst. Rubber Ind.* **29**, 297 (1952)) are slightly in excess of van den Tempel's figure. In view of the limited relative accuracy of the small intercept P for natural latex (2 ± 0.5 per cent), a full-size analysis of our natural latex did not seem warranted.
- ⁸ Kern and Kern, *J. Applied Physics* **21**, 705 (1950).
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- ¹⁰ Electron diffraction experiments by the authors confirm that natural latex hydrochloride shows crystallinity (see van Veersen, *Proc. 2nd Rubber Technol. Conf. London*, **1948**, p. 87), whereas synthetic polyisoprene hydrochloride is amorphous (see D'Ianni, Naples, Marsh, and Zarney, *Ind. Eng. Chem.* **38**, 1178 (1946)).

AGING STABILITY OF NEOPRENE LATEX. RELATION BETWEEN CROSS-LINKING AND HYDROLYSIS OF ALLYLIC CHLORINE *

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Elastic films prepared from Neoprene latex are strengthened and made more resilient by curing. The curing temperature must be high enough to activate certain cross-linking reactions which connect the polymer molecules in a three-dimensional network. Empirical evidence suggests that these cross-linking reactions are affected by the age of the latex from which the films are made, since without accelerators the tensile strength of the films declines as the latex ages. The reactions differ from cross-linking in natural rubber, since technically acceptable cures are obtained without using sulfur as a compounding material¹.

The present paper considers both of these effects by describing the changes in the chemical structure of the polymer in Neoprene latex particles which occur as the latex ages. These changes are then related to the decline in tensile strength and to the mechanism of cross-linking. The tensile strength of films from old latexes can be maintained at optimum levels by the proper choice of compounding materials.

MATERIALS AND METHODS OF TEST

Technical grade 2-chloro-1,3-butadiene (chloroprene) freshly distilled from a 50:50 chloroprene-toluene mixture was used to prepare the latexes. The chloroprene was 99% pure and contained less than 0.3% dichlorobutene and 0.12% methyl vinyl ketone (3-buten-2-one). Other materials included commercial N-wood rosin (about 90% abietic acid) and 97% sodium hydroxide.

Compounding materials were hard clay (Suprex clay having the composition 44% SiO₂, 38% Al₂O₃, 1.6% Fe₂O₃, and 0.9% Li₂O), antioxidant (Neozone-D, N-phenyl-2-naphthylamine, phenyl-2-naphthylamine), rubber grade zinc oxide, accelerators [Thiuram-E, bis(diethylthiocarbamyl) disulfide, tetraethylthiuram disulfide], and (Tepidone, sodium dibutylidithiocarbamate).

Unless otherwise noted, the latex used in all experiments was a 100% conversion emulsion polymer dispersed in water to a total solids content of 50% by weight. The polymer was sulfurmodified—that is, its molecular weight and plasticity were controlled by the addition of sulfur before polymerization.

Aging cycles of the latex were accelerated by heating at 90° ± 1° C. Each sample, contained in a tightly capped flask which had been flushed with nitrogen before filling, was exposed to air only during transfer from reaction vessel to aging flask. Oxidation effects were shown to be negligible by comparing infrared carbonyl oxidation bands before and after aging. Samples were aged for 0, 4, 8, 16, 24, and 48 hours.

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 47, No. 1, pages 171-176, January 1955. This paper was presented before the Division of Rubber Chemistry of the American Chemical Society at the meeting of the Division in Louisville, Kentucky, April 14-16, 1954.

The concentration of chloride ions in the water phase and the quantity of active chlorine in the polymer phase were determined by methods previously described².

Thin films were prepared by drying the latex on a glass plate for several minutes at 50° C. The films were leached overnight to remove soap, catalyst, and other water-soluble materials, and then vacuum-dried. Spectra were obtained on a Perkin-Elmer Model 21 double-beam infrared spectrometer. Differences in film thickness were adjusted by using the 8.15-micron band as a relative measure of thickness.

Latexes were compounded with zinc oxide, clay, and phenyl-2-naphthylamine in the ratio of 100 parts of dry polymer to 5 parts of zinc oxide, 10 parts of clay, and 2 parts of antioxidant. These materials were introduced as 50% by weight dispersions. Before compounding, the pH of all latexes was adjusted with 2% sodium hydroxide, so that it required 3.5 meq. of hydrochloric acid to lower the pH to 10.5 for each 100 grams of latex. After dipping, the films were leached for 2 hours in ion-free water and dried for 24 hours at room temperature and finally for 4 hours at 70° C. This process is known as zero cure. Some cross-links are formed during the drying cycle, so that zero-cured films are partially vulcanized. Selected films were cured for 30, 60, and 120 minutes at 141° C in addition to drying. Tensile strengths were obtained from films about 18 mils thick, using Die C, according to the ASTM D 412-51T specification.

Statistical tests³ showed that these measurements are reproducible to about ± 300 pounds per square inch based on the unstretched cross-sectional area of the films.

Swelling measurements were made according to Whitby's technique⁴. The initial volume of an unswelled sample was taken as the volume of Neoprene in the sample, calculated from the compounding formula.

SWELLING THEORY

The swelling measurements were interpreted in terms of Flory-Rehner theory⁵, using the solubility parameters and a polarity factor determined for Neoprene by Scott and Magat⁶.

The basic equation is:

$$M_c' = \frac{\rho V v_2^{\frac{1}{2}}}{-\left[\ln(1 - v_2) + v_2 + \mu v_2^2\right]} \quad (1)$$

where

$$\mu = \mu_s + \frac{KV(S_0 - S_r)^2}{RT}; \mu_s = 0.3 \quad (2)$$

A more recent derivation of the relation⁷ between swelling volume and M_c' has not been used, since the entropy of elasticity, on which this relation is based, is in dispute⁸.

The value for μ , applies to most rubber-solvent systems and is equal to $1/\alpha$ where α is the coordination number—that is, the number of neighbor sites around each site in the latex set up to calculate the entropy of mixing. Alpha has been estimated⁹ to be 3 or 4, so that some small uncertainty is introduced in the magnitude of M_c' . A value of 0.44 has been found for μ for natural rubber swollen in benzene¹⁰, while for Neoprene in toluene $\mu = 0.322$, when calculated according to Equation 2.

It has been pointed out by Flory¹¹ and Fletcher and associates¹² that M_e' is only the apparent molecular weight between cross-links. Corrections must be applied to allow for mechanical entanglements and for chain ends which lie outside the network, and therefore do not contribute to the elastic properties.

These corrections have the form:

$$\frac{1}{M_e'} = g \left(\frac{1}{M_e} - \frac{2}{M} \right) \quad (3)$$

Mochel¹³ has shown that 100% conversion, sulfur-modified Neoprene polymers are essentially all gel at low conversions (about 40%), which makes it experimentally difficult to determine the primary molecular weight, M . From the results on sol polymers¹⁴ it can be estimated that the uncross-linked molecular weight is at least 200,000. M_e' is, therefore, greater than M_e by 10% or less.

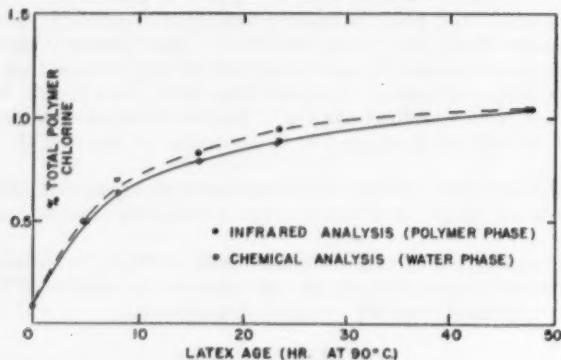
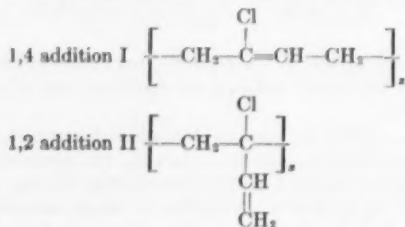


Fig. 1.—Chloride ions in water phase of Neoprene latex.

In the absence of any data on g , it was assumed to be 1—that is, entanglements which act to prevent swelling are counted as true covalent crosslinks.

CHANGES IN STRUCTURE DURING AGING

At 40° C, polychloroprene polymer chains grow mainly by the 1,4 addition (I) of chlorobutadiene free radicals¹⁵, although about one monomer unit in 67 (1.5 mole-%) enters the growing chain by 1,2 addition (II)¹⁶.



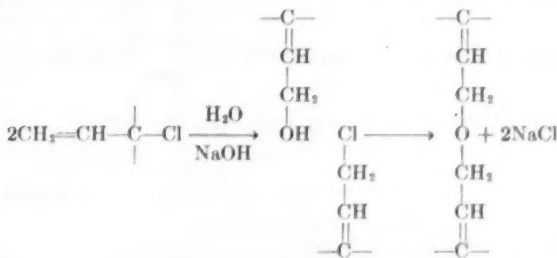
The chlorine in the 1,2-structure is very reactive and, in a latex, readily undergoes alkaline hydrolysis, with elimination of chloride ion. This halogen is

eventually found in the water phase of the emulsions as hydrochloric acid or sodium chloride, in the quantities shown in Figure 1.

Changes in the intensity of a strong absorption band in the infrared at 10.8 microns, corresponding to changes in the structure of the terminal olefinic group of the 1,2-structure¹⁷, indicate that these 1,2-sites are the chain positions from which the aqueous chloride originates. When this band is calibrated, the percentage of the total content of the polymer chlorine which is evolved as chloride ions can be calculated from the decrease of absorption of the terminal olefinic group. Good agreement is found between this calculation and the direct determination of chloride ions in the aqueous phase, as shown in Figure 1. The calibration is made by equating the depth of the band to the percentage of allylic chlorine initially found in the polymer by chemical analysis. This calibration is believed to be valid, since both the infrared and chemical techniques give the same amount of allylic chlorine when the infrared absorption is calculated with 3-chloro-1-butene¹⁸. Not only do the infrared data confirm the association of the released chlorine with the structure from 1,2-addition, but they also show that the double bond shifts during the reaction, as such a bond rearrangement is necessary to make the absorption diminish in intensity as the hydrolysis proceeds.

The rate of halogen evolution is independent of the initial concentration of chloride up to 0.215*M*, as well as of the initial concentration of hydroxyl ions, as shown in Figure 2. Neither the *S_N1* nor the *S_N2* mechanism proposed for the nucleophilic substitution of alkyl halides would predict such behavior¹⁹. Unfortunately, the observed rate of the reaction provides no information on the mechanism, as it fits neither first- nor second-order kinetics. Presumably the rate is affected by the diffusion of ions into and out of the latex particles. The data, however, are in accord with an intramolecular rearrangement accompanied by hydrolysis, similar to the mechanism suggested for the solvolysis of α,α -dimethylallyl chloride (3-chloro-3-methyl-1-butene)¹⁹.

When allyl halides hydrolyze they ordinarily produce alcohols. However, further reaction may occur, especially at high pH, to give diallyl ethers²⁰. In Neoprene, the formation of an ether would result in a cross-link by a mechanism of the type:



The proposed cross-linking mechanism indicates that two chlorine atoms are released as ionic chlorine, and two chains of molecular weight M_c' are formed, for each cross-link introduced by hydrolysis. As each monomer unit in Neoprene contains one chlorine atom, the number of chlorine atoms in a chain is found by dividing the molecular weight of a chain, M_c' , by the molecular weight of one monomer unit, M_μ . The fraction of chlorine atoms separated from the polymer by cross-link formation will be $2/2(M_c'/M_\mu)$. This fraction was deter-

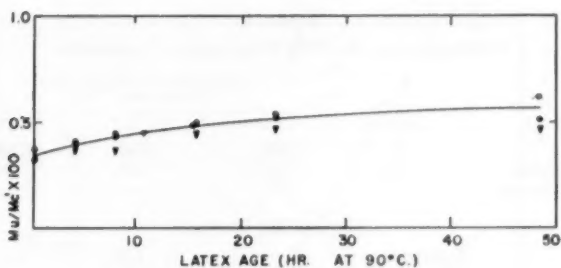


FIG. 3.—Swelling of uncured Neoprene films.

▼ Film alone
○ With zinc oxide
● With zinc oxide and clay

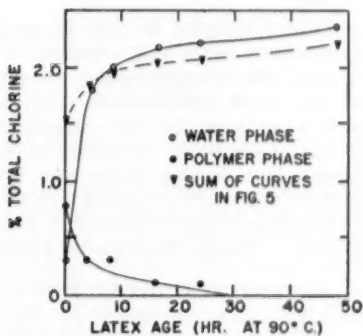


FIG. 4.—Active halogen in Neoprene latex with excess piperidine.

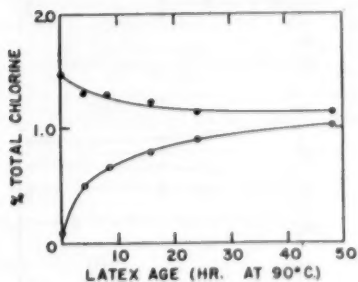


FIG. 5.—Active halogen in Neoprene latex.

● Polymer phase
○ Water phase

VULCANIZATION AND TENSILE STRENGTH

In order to determine the effect of these aging changes on the physical properties of dipped films, it is necessary to know what structural changes occur during vulcanization. It is thought that cross-linking takes place between active chlorine chain positions during cure, as well as during aging. Evidence

TABLE I
VULCANIZATION OF 70% CONVERSION NEOPRENE

Polymer	% Cl removed	300% Modulus (lb./sq. inch) (Cure, min./° C)		
		10/153	20/153	40/153
Untreated	0	2050	2500	3150
Piperidine treated (80° C/14 hours)	1.5	370	350	450

Compounding Recipe

Polymer	100
SRF carbon black	30
Magnesia	4
Zinc oxide	5
Ethylene thiourea	1
N-Phenyl-1-naphthylamine	1.6

for this is provided by the vulcanization of a low conversion Neoprene treated with piperidine to remove most of its labile chlorine. The data in Table I apply to the polymer treated with a large excess of piperidine at 80° C and subsequently compounded on a mill. The results show that, when the active chlorine content of the polymer is significantly reduced, the polymer cannot be cured satisfactorily by normal Neoprene vulcanization techniques.

To study the changes in cross-linking during cure, films were dipped from latexes of various ages and various compounding formulas. These films were cured and tested for both stress-strain relationships and the extent of cross-linking as measured by swell. The swelling results, shown in Figure 6, lead to

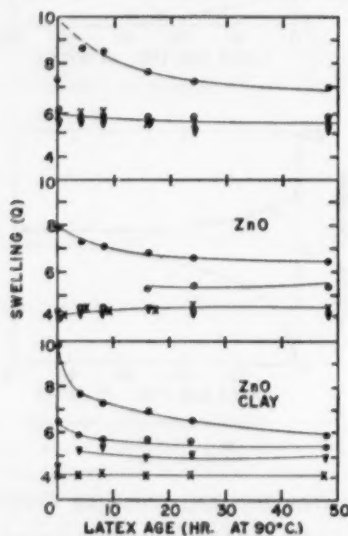


FIG. 6.—Swelling of Neoprene in toluene at 25° C. Cure minutes at 141° C.

● 0
○ 30
▼ 60
× 120

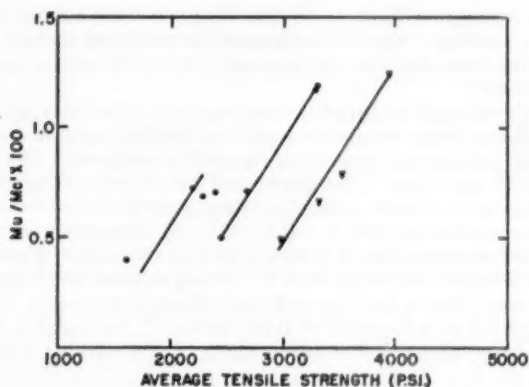


Fig. 7.—Relation of crosslinks to tensile strength.

- No zinc oxide or clay
- Zinc oxide
- ▼ Zinc oxide and clay

the important conclusion that only a limited number of cross-links are possible in Neoprene films.

This limit is reached after a 30-minute cure at 141° C for films not containing compounding materials. Further heating for 1 or 2 hours introduces no additional cross-links. The limit is raised and is reached only after a 60-minute cure for films compounded with zinc oxide. The limiting Q values correspond to a release of 0.70% of the total chlorine in the first case, and 1.1% of the total chlorine in the second case, calculated according to the Flory-Rehner theory and the procedure described previously.

An empirical relation between the ratio $M\mu/M_c' \times 100$ and the tensile strength is graphed in Figure 7. A similar relation has been reported for natural rubber²¹. The tensile strength of cured Neoprene samples, for a given compounding formula, is a linear function of the percentage of monomer units engaged in cross-linking within the range studied. When the number of cross-links remains constant during an increase of curing time, the tensile strength also remains constant. The addition of a clay filler causes a large over-all rise

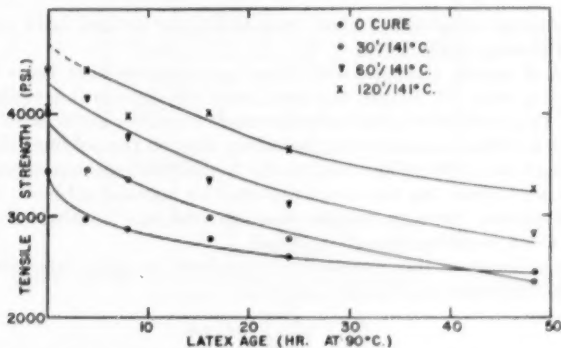


Fig. 8.—Decline in tensile strength with latex age. Compound: zinc oxide and clay.

of the tensile strength without a corresponding rise of the number of cross-links, measured by swelling. Such a result would be produced through the destruction of bonding forces between polymer and clay by the spreading action of the absorbed solvent²³.

The tensile strength is also an inverse function of the latex age, as shown in Figure 8. When these tensile strengths are plotted against cross-linking, a linear relation, such as that graphed in Figure 7, is not found. For example, the total number of cross-links in the films cured 120 minutes is independent of the latex age, whereas the tensile strength of these same films declines continuously. The level of cross-linking after a 120-minute cure apparently corresponds to a plurality of tensile strengths, in contradiction to the data of Figure 7.

The contradiction can be removed by making a distinction between the total number of cross-links in the film and the "effective number". The total, X , may be expressed as a function of three terms: F , the number of cross-links between allylic positions formed during aging; P , the number of cross-links be-

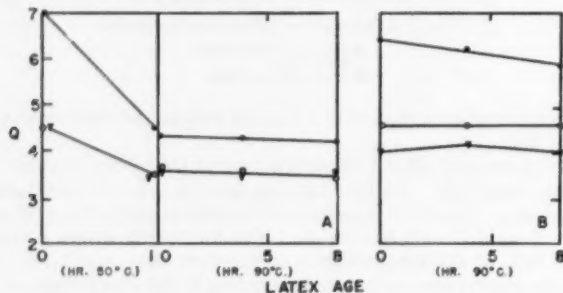


Fig. 9.—Swelling of films compounded with zinc oxide and caprolactam. A. Heating plus compounding. B. Heating and compounding. Cure, minutes at 141° C.

● 0
○ 30
▼ 60 and 120

tween allylic positions formed during cure; and Y , the number of cross-links between RCl positions during cure. More explicitly, X is given by:

$$X = F(T, t) + [P(N, F, R, T', t') + Y(T', t')] \quad (4)$$

This equation emphasizes that cross-links are formed both during cure (P, Y) and during aging (F).

The fall of tensile strength with latex age suggests that those cross-links formed during cure (P, Y) are the ones most effective in determining tensile strength. These effective cross-links decrease in number as the latex ages, since there is only a limited number of cross-linking sites on the polymer chain and an increasing number of these are used in the hydrolysis reaction during aging.

A "preure" effect has also been reported for natural rubber²³, so that the inverse correlation between tensile strength and the number of cross-links within the latex particles appears justified.

Further evidence of this correlation is obtained by aging latex samples containing ϵ -thiocaprolactam (III),



TABLE II
AVERAGE TENSILE STRENGTH FOR VARIOUS CURES

Cure (min./° C)	Av. tensile strength (lb./sq. inch)		
	A	B	C
0/0	3490	3091	1580
30/141	3690	3610	1840
60/141	4260	4110	2420
120/141	4240	4140	2480

Compounding Recipe

- A. ZnO-5, clay-10
 B. ZnO-5, clay-10, ϵ -thiocaprolactam-2 (heating + compounding)
 C. ZnO-5, clay-10, ϵ -thiocaprolactam-2 (compounding + heating)

a compound which can react at both the sulfur and nitrogen positions with active chlorine in the polymer. In this case cross-links may be formed in the latex particles, both by hydrolysis and by reaction with ϵ -thiocaprolactam. The number of these cross-links is measured by swelling uncured films. Such measurements, shown in Figure 9, A, indicate that the intraparticle cross-linking increases rapidly with the age of the treated latex. In a very short time a limiting cross-link density, corresponding to a Q of 4.2, is reached. This limit is almost as great as that found in a fully cured film prepared from an untreated latex. The films from the latex containing ϵ -thiocaprolactam become even more tightly cross-linked on curing, as indicated by a decrease in the swelling to a Q of 3.5.

As a result of the highly cross-linked particles in the treated latex, there is a drastic decline of tensile strength, as shown in Table II, recipes A and C.

If ϵ -thiocaprolactam is added to a previously aged latex, in addition to other compounding materials, it has no effect on either the final cross-link limit or the tensile strength. For swelling, these data are given in Figure 9, A, to be compared to the zinc oxide-clay cure in Figure 6. For the tensile strengths, recipes A and B may be compared. It is evident, however, that the same cross-link distributional effect is operating on an accelerated basis, providing further evidence that the tensile strength of dipped films is in part determined by the distribution, as well as the number, of cross-links.

Certain compounding materials prevent the tensile strength decline¹. Tetraethylthiuram disulfide, as indicated in Figure 10, or combinations of

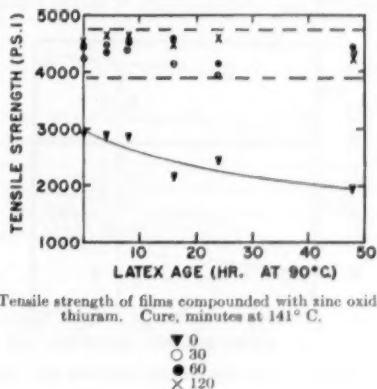


Fig. 10.—Tensile strength of films compounded with zinc oxide, clay, and thiuram. Cure, minutes at 141° C.

▼ 0
 ○ 30
 ● 60
 × 120

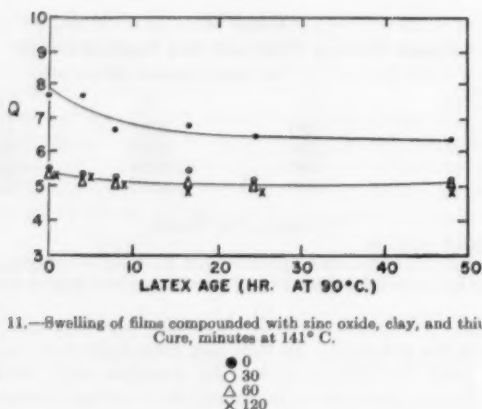


FIG. 11.—Swelling of films compounded with zinc oxide, clay, and thiuram. Cure, minutes at 141°C.

thiuram, sodium dibutyldithiocarbamate, and sulfur are very effective in this respect. The equilibrium swelling of films compounded with thiuram is slightly greater than the swelling of films containing only zinc oxide. Q is about 5 compared to 4.1 (Figure 11). This difference indicates that the films containing thiuram and zinc oxide are less cross-linked than films containing only zinc oxide.

Although there are not enough data to allow a definite conclusion concerning the action of tetraethylthiuram disulfide, it appears that the thiuram is cleaving the polysulfide links in the polymer molecules, which, by some unknown mechanism, improves the tensile strength. A similar cleavage effect has been found in the breakdown of sulfur-modified Neoprenes by treatment with thiuram²⁴.

The changes of composition of polychloroprene with latex age are reviewed in Figure 12. The amount of polymer chlorine released during cross-linking is given by the lowest curve, 1. Next is the amount of chloride ion found in the aqueous phase, 2. The difference is presumed to be the amount of allylic chlorine converted to alcohol during hydrolysis. The straight line, 3, represents the total amount of allylic chlorine initially present, and the upper line, 4, is the amount of chloride ion found in the water phase when piperidine is present. This latter curve measures the total amount of labile chlorine in the polymer.

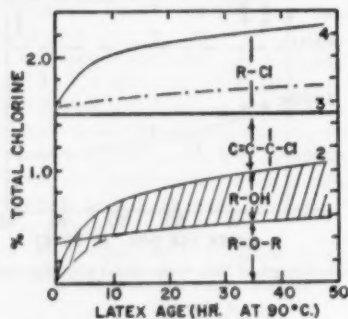


FIG. 12.—Changes in composition of Neoprene polymer with latex age. From Figures 3, 4, and 5.

The amount of labile chlorine available for cross-linking will be given by 4 minus the quantity of allylic chlorine converted to alcohol—i.e., the crosshatched portion. This difference is almost constant at about 1.6% of the total chlorine.

The data suggest that, during cure without compounding ingredients, only the allylic chlorines enter into cross-linking and about 0.70% of the total chlorine content of the polymer is used (A, Figure 13). When zinc oxide or zinc oxide plus an accelerator is added, all the labile chlorine becomes available and the cross-linking increases to use about 1.1% of the total chlorine (B and C, Figure 13). If the accelerator is added before aging, it can react rapidly with most of the allylic chlorine to a limit of 1.05% (E, Figure 13, and Figure 8), suppressing the hydrolysis reactions. On further cure (D, Figure 13) the cross-linking limit rises to about 1.8% chlorine with the utilization of the RCl-active sites.

SUMMARY

Neoprene polymer chains are cross-linked between active chlorine sites on the chains. There are two types of active sites of different reactivity. It is

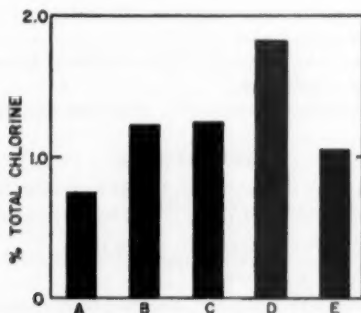


FIG. 13.—Released chlorine limit in cured films. A. Uncompounded. B. Zinc oxide. C. Zinc oxide and ϵ -thiocaprolactam after aging. D. Zinc oxide and ϵ -thiocaprolactam before aging. E. Zinc oxide and ϵ -thiocaprolactam before aging, 0 cure.

necessary to use more vigorous curing conditions to actuate the less reactive chlorine. The polymer develops cross-links while aging as a latex as well as during cure, and the decline of tensile strength with latex age may be inversely correlated with the amount of cross-linking during aging. The decline of tensile strength can be prevented by compounding with bis(diethylthiocarbamyl) disulfide.

The calculations of the swelling data are not so complete as might be desired, primarily because of difficulty of measuring and interpreting the molecular weight of high-conversion polymers and to some uncertainty in determining μ . It is felt that the qualitative observations are justified, and that they serve to define both the technically important effect of film structure on tensile strength and the mechanism of cure.

ACKNOWLEDGMENT

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NOMENCLATURE

- M_c' = apparent molecular weight between cross-links
 v_2 = volume fraction of rubber
 Q = volume of solvent absorbed per unit volume of polymer = $(1 - v_2)/v_2$
 V = molar volume of solvent (107 for toluene)
 ρ = density of polymer (1.23 for Neoprene)
 K = polarity factor [1.0 for Neoprene²⁶]
 S_m = solubility parameter for Neoprene [9.25 at 25° C²⁵]
 S_0 = solubility parameter for solvent [8.9 for toluene at 25° C²⁵]
 M_c = true molecular weight between cross-links
 M = molecular weight of uncross-linked polymer molecules
 g = parameter (1 to 10) representing effect of entanglements
 T = temperature of latex aging
 t = time of latex aging
 T' = temperature of cure
 t' = time of cure
 N = total number of allylic positions
 R = number of allylic positions converted to OH
 F = total number of cross-links
 P = number of cross-links between allylic positions formed during cure
 X = total number of cross-links
 Y = number of cross-links between RCl positions during cure

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MECHANISM OF FORMATION OF CREAM IN GR-S LATEX *

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Many high-solids GR-S latexes, especially those made at temperatures near 0° C, form a thick cream on the surface if allowed to stand without agitation for a sufficient length of time. Although this material can be redispersed, the tendency toward cream formation is undesirable because it results in non-uniformity if the latex is not continuously agitated; furthermore, the presence of cream is deleterious to the physical properties of films formed from latex¹.

From calculations based on Stokes' law, it is readily evident that the particles constituting cream must be relatively huge, since the numerical bulk of the particles in cold, high-solids GR-S latexes, which are usually in the range of diameters 800 to 2000 Å, will not rise fast enough under the influence of gravity to form significant amounts of cream. If a typical high-solids GR-S latex is diluted to about 5 per cent solids, so that its viscosity approaches that of water, particles 100,000 Å in diameter will rise at the rate of about 1 cm. per hour; particles 20,000 Å in diameter will rise about 1 cm. a day; if the particle diameter is 1000 Å, the theoretical rate of rise is roughly 1 cm. per year. Since a particle 20,000 Å in diameter weighs 8000 times as much as a particle 1000 Å in diameter, the formation of cream is indicative of the presence of comparatively enormous particles. Cream may well be considered as incipient coagulum; however, cream can be redispersed, while coagulum cannot. This difference makes possible the use of latexes containing as much as 5 or even 10 per cent by weight of the larger but microscopic particles of the type which form cream, while no more than 0.2 or 0.3 per cent of coagulum is ordinarily tolerable. Thus, cream is undesirable in the sense that it is harmful to the properties and uniformity of the latex, but it can often be tolerated in appreciable concentrations, whereas coagulum must be removed. It is, therefore, an important factor to be considered in latex polymerization, and a study of the mechanism of formation of large particles has appeared desirable.

Among the possible mechanisms of cream formation which were considered were: that the agglomeration to giant particles in cold, high-solids latex occurs on the surfaces of the reaction vessel, which in large reactors are at a lower temperature than the polymerizing mixture; that polymerization within the relatively large monomer droplets accounts for the formation of the giant particles; or that under certain conditions an insufficiency of soap during the polymerization results in the formation of large particles, rather than coagulum.

The work described in this paper was carried out with a single type of latex, and mild agitation was used in the polymerizations, contrasted with the vigorous agitation in plant reactors. However, some of the principles governing cream formation under these mild conditions of agitation have been applied success-

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fully to large scale production. It appears somewhat unlikely that entirely different mechanisms of cream formation are operative in different high-solids GR-S recipes, which are basically very similar. However, the exact measures to be employed in eliminating cream may well vary considerably.

MECHANISM OF CREAM FORMATION

To study the mechanism of cream formation, certain variables were investigated in small-scale polymerizations carried out in 24-ounce pressure bottles. A method for determination of particle-size distribution based on Stokes' law² provided a rapid and quantitative means of estimating the creaming tendency of various latexes. Essentially the method consists of determining the decrease of solids content at various heights, and after various time intervals, in the highly diluted latex. Particle-size distribution is calculated from the data by means of Stokes' law. While it is necessary to centrifuge for analysis of small particle sizes, gravitational separation sufficed for the determination of the very

TABLE I
POLYMERIZATION FORMULA FOR J-2820 LATEX

Butadiene	70
Styrene	30
Water	70 ^a
Diisopropylbenzene hydroperoxide	0.22
Mixed soap ^b	1.25
Dispersing agent ^c	1.5
Ferrous sulfate heptahydrate	0.09
Sodium hydrosulfide	0.039
Potassium sulfate	0.4
Potassium pyrophosphate	0.25
<i>tert</i> -Dodecanethiol	0.1

Except where otherwise indicated, polymerizations were carried out for 48 hours in 24-ounce pressure bottles. In most cases 300 grams of monomers were charged; 1.75 parts of potassium oleate are ordinarily added during the polymerization, as an 18% solution, when conversion of monomers has reached 35%. Polymerization temperature was 5° C.

^a In large scale production 60 parts of water are used.

^b Potassium salt of a heat-treated, distilled fraction of tall oil; ratio of fatty to rosin acid, about 5 to 3 by weight.

^c Potassium salt of condensed alkyl naphthalenesulfonic acid.

large particles of interest here. The only significant change in technique² was the use of 1 per cent ammonium alginate rather than 0.4 per cent. The 1 per cent alginate is mixed with an equal volume of latex for the purpose of obtaining separation between serum and polymer in order to determine polymer density. This higher concentration was found necessary to give complete separation in many of the latexes prepared for this work.

J-2820, a cold high-solids latex activated by ferrous sulfide, was chosen as the basis for the work because, as produced at the time of these experiments, it ordinarily contained a relatively high concentration of very large particles (5 to 10 per cent by weight). The polymerization recipe for J-2820 latex is given in Table I. As indicated, 1.75 parts of potassium oleate, per 100 parts of charged monomers, are ordinarily added as an 18 per cent solution when the conversion of monomers has reached 35 per cent. The data in Table II show that a large proportion of the weight of polymer in the latex consists of giant particles when the stabilizing soap is omitted from the recipe, and that small variations in the amount of the mixed soap derived from tall oil, and of dispersing agent present, have little effect. A more complete description of the

TABLE II
CONCENTRATION OF LARGE PARTICLES IN UNSTABILIZED J-2820 LATEX
MADE WITH VARYING AMOUNTS OF SOAP AND DISPERSING AGENT^c

No.	Mixed soap ^a (parts)	Dispersing agent ^a (parts)	Final conversion of monomers (%) ^b	Wt.-% of particles over 20,000 Å in diameter ^c
1	1.1	1.5	38	29.8
2	1.2	1.5	46	33.8
3	1.25 ^d	1.5 ^d	46	44.0
4	1.3	1.5	46	39.6
5	1.4	1.5	49	31.8
6	1.25	1.3	47	36.8
7	1.25	1.4	45	34.7
8	1.25	1.6	47	33.7
9	1.25	1.7	41	30.3

^a Per 100 parts charged monomers. For chemical description see Table I.

^b Polymerized 24 hours instead of usual 48.

^c Mean of duplicate results on stripped latexes. Less than 2% coagulum present in each latex.

^d Amount ordinarily present in J-2820 latex.

soap and dispersing agent is given in Table I. The soap is referred to hereafter simply as mixed soap.

In order to determine at what stage in the reaction these large particles are formed, a series of polymerizations was carried out in which the reaction was shortstopped after varying degrees of polymerization had taken place (Table III). The particles over 20,000 Å in diameter begin to appear between 18 and 34 per cent conversion of monomers. The data in the fifth and sixth columns show that, at 34 per cent conversion, these particles are mainly between 20,000 and 100,000 Å in diameter. Particles smaller than 20,000 Å were not investigated. As the polymerization proceeds, increasing amounts of polymer particles over 100,000 Å in diameter appear, but the amount of material between 20,000 and 100,000 Å in diameter remains nearly constant. The total concentration of large particles, therefore, increases with increasing conversion.

There is a continuous formation of particles in the 20,000 to 100,000 Å range, which continue to grow as the polymerization proceeds, so that more and more material appears in the range of diameters greater than 100,000 Å. The fact that the concentration of particles in the 20,000 to 100,000 Å range remains nearly constant in the later stages of polymerization, despite the growth of many particles to a diameter greater than 100,000 Å, indicates that continuing

TABLE III
VARIATION OF LARGE PARTICLE CONCENTRATION WITH CONVERSION IN
UNSTABILIZED J-2820 TYPE LATEXES

No.	Final conversion of monomers (%)	Particles (wt.-%)		Wt. of polymer (grams)		
		Over 100,000 Å in diameter ^a	Between 20,000 and 100,000 Å in diameter ^a	Over 100,000 Å in diameter ^b	Between 20,000 and 100,000 Å in diameter	Over 20,000 Å in diameter
1	14	0	0	0	0	0
2	18	0	0	0	0	0
3	34	5.4	26.8	3.7	18.2	21.9
4	38	1.5	20.5	1.1	15.6	16.7
5	41	21.5	19.1	17.6	15.7	33.3
6	48	15.4	15.9	14.8	15.3	30.1
7	53	23.5	19.1	24.9	20.2	45.1

^a Mean of duplicate results on stripped latexes. Less than 2% coagulum present in each case.

^b 200 grams of monomers charged in each polymerization.

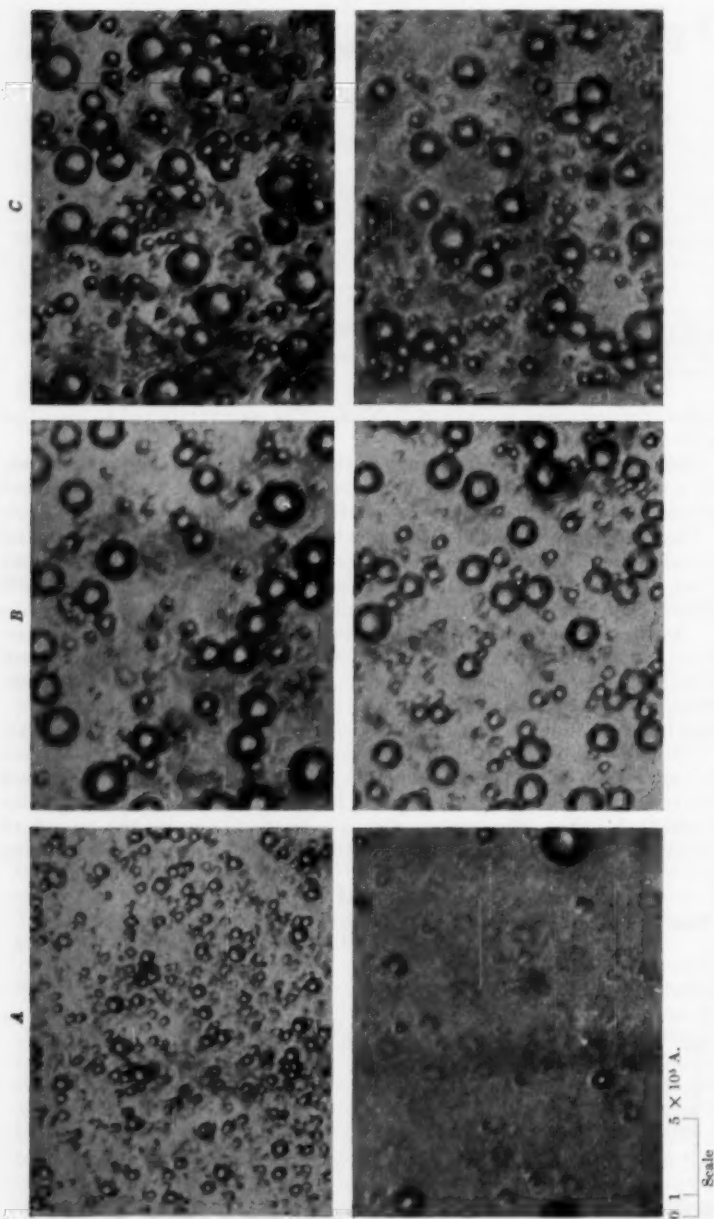


FIG. 1.—Photomicrographs of unstabilized 1-2820 latexes shortstoped at various conversions. A, 14% conversion. B, 34% conversion. C, 53% conversion. Latexes diluted to solids content of 2% before photographing. Magnification, 850 X. Upper row, Unstripped latexes. Lower row, Stripped latexes.

growth or agglomeration of small particles occurs as the polymerization proceeds, thus replenishing the quantity of particles in the intermediate range.

A second possibility is that the growth or agglomeration to sizes between 20,000 and 100,000 Å occurs preferentially in the early part of the polymerization, while direct growth of small particles to sizes greater than 100,000 Å is favored in the later stages. As there is no particular reason for assuming such a change, with increasing conversion, in the mechanism of growth, the hypothesis of a gradual and continuous increase in size appears somewhat more plausible.

The approximate time of formation of large particles, and the increase of particle size with increasing conversion, are confirmed by the photographs in Figure 1 taken of latexes shortstopped at 14, 34, and 53 per cent conversion.

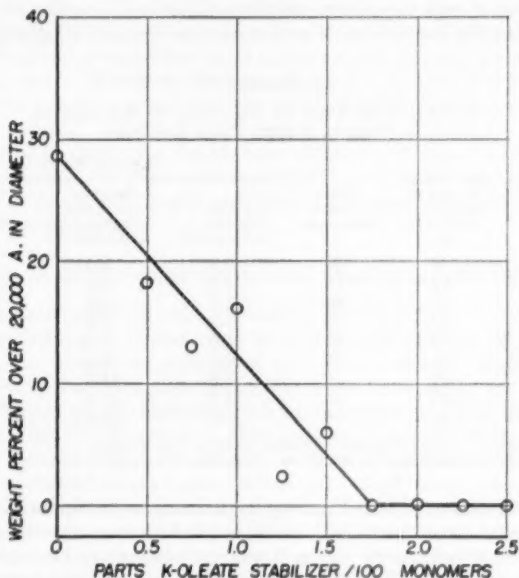


FIG. 2.—Effect of varying amounts of stabilizing soap on large particle content of J-2820 latexes. Stabilizer added when conversion of monomers had reached $36 \pm 6\%$ in each case.

A sample of each latex, after dilution to a solids content of 2 per cent, was photographed on a Levy microscope slide of the type used for blood counts. The use of this type of slide ensures the inspection of a constant volume of latex, and the rulings permit ready calibration of the magnification. Another fact evident from the photographs is that a large group of particles, about 5000 to 15,000 Å in diameter, present in the unstripped latex of 14 per cent conversion, is not observed in the same latex after stripping, or in the stripped or unstripped latexes of 34 and 53 per cent conversion. The particles are probably emulsified droplets of monomer which are removed on steam stripping, or which dissolve in the polymer particles at higher conversion (at low conversion there is insufficient polymer present to dissolve all the monomer, since the polymer can dissolve only one to two times its own weight of monomer).

The data plotted in Figure 2 show the effect of varying amounts of added stabilizing soap on the formation of very large particles. In each case the soap was added at a conversion of 36 ± 6 per cent. It is evident that the proportion of such particles decreases as the quantity of stabilizer is increased. No appreciable weight of particles over 20,000 Å in diameter was found when the amount of stabilizing soap exceeded 1.75 parts, i.e., when the total soap content exceeded 3.0 parts. The conversion of monomers at the time of addition of the 1.75 parts of soap was 31 per cent. This quantity of stabilizer is ordinarily used in making J-2820 latex.

The data presented so far show that large amounts of giant particles form during polymerizations carried out without the addition of stabilizing soap, that the formation of these particles begins between 18 and 34 per cent conversion, and that it can be minimized by addition of a sufficient quantity of stabilizer when the conversion of monomers has reached 36 ± 6 per cent.

TABLE IV
VARIATION IN TIME OF ADDITION OF STABILIZING
SOAP IN J-2820 TYPE LATEXES

No.	Conversion at time of addition of stabilizer* (%)	Final conversion of monomers (%)	Particles, Wt.-%		
			Over 100,000 Å in diameter ^b	Between 20,000 and 100,000 Å in diameter ^b	Over 20,000 Å in diameter
1	8	94	0.5	2.5	3.0
2	12	89	2.5	0.9	3.4
3	12	89	1.5	0.5	2.0
4	19	98	1.9	2.0	3.9
5	29	61	1.0	7.3	8.3
6	31	56	0.5	8.1	8.6
7	41	59	2.0	14.2	16.2
8	46	59	4.5	17.5	22.0
9	53	56	5.0	26.6	31.6

* Usual stabilizer, 1.75 parts of potassium oleate, added as 15% solution.

^b Mean of duplicate results on stripped latexes. Less than 2% coagulum present in each latex.

These data suggested that the very large particles are formed by agglomeration of growing small particles, as their total surface area increases during polymerization to an extent where it cannot adequately be protected by the soap initially present. This would explain the fact that the large particles do not appear until polymerization has attained sufficiently high conversion and that the addition of stabilizing soap prevents the formation of such particles (by providing the necessary surface coverage).

The data in Table IV show the effect of adding 1.75 parts of potassium oleate as stabilizer at varying conversions in a series of polymerizations. Few very large particles form if the stabilizer is added early enough in the polymerization (at a conversion of 19 per cent or less). An appreciable quantity of large particles, 8.3 per cent by weight, was present after stripping when the stabilizer was added at 29 per cent conversion, and this quantity increased to a maximum of 31.6 per cent as the extent of conversion at the time of addition of stabilizer increased.

While the final percentage conversion of monomers was increased when the stabilizing soap was added in the early stages of the polymerization, the corresponding reduction in the amount of large particles formed does not appear to be related to conversion. If these latexes had been shortstopped when the con-

version was lower, say 60 per cent, it seems certain that the same result—the absence of giant particles would have been obtained. The alternative—that large particles are redispersed into small particles at high conversions—appears very improbable.

These results are consistent with the data obtained by varying the extent of conversion in unstabilized latexes. The fact that it is necessary to add stabilizer early in the polymerization in order to prevent formation of giant particles is consistent with the finding that such particles do not form until conversion has reached 18 to 34 per cent. Thus, if the stabilizer is added too late, agglomeration has already occurred, and the stabilizer is ineffective.

There is some inconsistency between these data and the data in Figure 2. Some large particles were formed in this series of experiments when the stabilizer was added at 29 per cent conversion, whereas the data in Figure 2 indicate that the same amount of stabilizer entirely prevents the formation of the large particles, even when added somewhat later in the polymerization (31 per cent conversion in this case). However, the percentage of large particles formed in the former case was not very large (8.3 per cent), and the discrepancy is readily attributable to normal variations among replicate polymerizations. The significant features of the data are the absence of large particles at low conversions in unstabilized latexes, or when stabilizer is added early, and the large quantity of such particles which are present at high conversions in unstabilized latex, or when stabilizer is added late.

EFFECT OF ROSIN SOAP ON LARGE PARTICLE FORMATION

The above data indicated that prevention of cream formation is essentially a matter of providing sufficient soap to protect the surfaces of the growing particles. It was, therefore, considered that the formation of giant particles might be prevented, without adding stabilizing soap during the polymerization, by the use of a soap which initiates fewer particles per unit of surface-covering capacity than does the mixed soap ordinarily used in J-2820 latex. Then, if the amount of this new soap is increased to such an extent that the same number of particles are initiated as are formed in normal J-2820 latex, more surface protection would be provided per particle. As the total surface area at a given conversion depends on the number of particles, this would result in a higher percentage coverage of the total surface area during polymerization. If sufficient improvement were obtained, it might be possible to polymerize without additional stabilizer. This would be of practical, as well as theoretical interest, since the addition of stabilizer at a definite conversion adds to the difficulties in large scale polymerizations.

Previous studies of reaction rates and latex viscosities have suggested that a unit weight of the potassium salt of a disproportionated rosin acid (rosin soap) initiates only about one-fourth to one-third as many particles, in J-2820 latex, as does the mixed soap ordinarily used. Also, it was found, by soap titration² of duplicate samples of the same latex, that the surface coverage of polymer per unit weight of mixed soap is only 25 per cent greater than that of the rosin soap. This indicated that the surface-covering capacity of the mixed soap per particle initiated is considerably less than that of the rosin soap. Therefore, to test the effectiveness of rosin soap in preventing large particle formation in un-stabilized J-2820 latex, a series of 24-ounce bottles of latex was prepared, in which the rosin soap was substituted for varying amounts of mixed soap. In the first series, substitution was made on the basis of 3 weight units of rosin

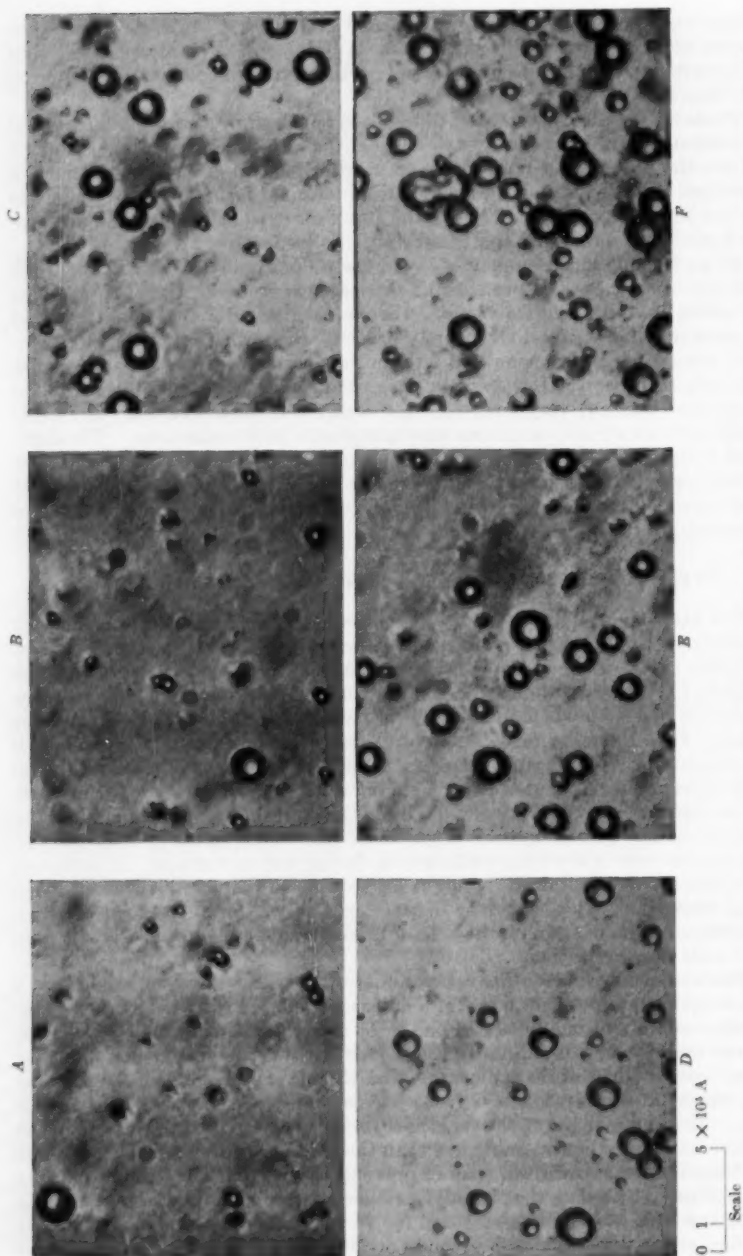


FIG. 3.—Photomicrographs of J-9820 latexes. 1.75 parts of potassium oleate added as stabilizer at various conversions. A. 13% B. 19% C. 29% D. 31% Latexes diluted to solids content of 2% before photographing. Magnification, 925 X.

soap for each unit of mixed soap removed. No stabilizer was added during the polymerizations. As shown in Table V, A, the percentage by weight of particles over 20,000 Å in diameter decreases as more rosin soap is substituted for mixed soap on this basis, i.e., as the total amount of soap increases. This percentage is zero when the total initial content of soap in the recipe is 2.85 parts or more.

Table V, B, shows the effects of substituting rosin soap for mixed soap on a 4 to 1 basis. Again, the percentage of very large particles decreases as increasing amounts of rosin soap are used, and is zero when the total soap content exceeds 2.75 parts. The use of larger quantities of mixed soap alone is not practical because it results in very viscous latexes of small particle size. However,

TABLE V
SUBSTITUTION OF ROSIN SOAP^a FOR MIXED SOAP^b
IN UNSTABILIZED J-2820 TYPE LATEXES

	No.	Mixed soap ^{b,c} (parts)	Rosin soap ^{a,b} (parts)	Final conversion of monomers (%)	Wt.-% over 20,000 Å in diameter ^d
A. Substitution on 3 to 1 basis	1	1.25	0	61	37.5
	2	1.15	0.3	64	27.2
	3	1.05	0.6	67	33.4
	4	0.95	0.9	70	28.3
	5	0.85	1.2	71	23.3
	6	0.75	1.5	66	20.4
	7	0.65	1.8	64	15.2
	8	0.55	2.1	56	11.6
	9	0.45	2.4	55	0
	10	0.35	2.7	54	0
	11	0.25	3.0	55	0
	12	0	3.6	55	0
B. Substitution on a 4 to 1 basis	1	1.25	0	61	37.5
	2	1.05	0.8	69	30.9
	3	0.95	1.2	56	8.3
	4	0.85	1.6	57	4.2
	5	0.75	2.0	58	0.0
	6	0.55	2.8	61	0.2
	7	0.35	3.6	65	0.0

^a Potassium salt of disproportionated rosin acid.

^b For chemical description, see Table I.

^c Per 100 parts charged monomers.

^d Mean of duplicate results on stripped latexes. Less than 2% coagulum present in each case.

two polymerizations were carried out in which the initial concentration of mixed soap was increased to 1.85 and 2.25 parts. The latexes were extremely viscous and contained 27.7 and 26.7 per cent by weight of particles over 20,000 Å in diameter, respectively, thereby indicating little improvement in stability. The use of a soap such as the rosin soap, which is relatively less effective in initiating particles, thus affords a practical method of eliminating cream without the addition of a stabilizing soap during the polymerization.

RELATION BETWEEN CREAM AND COAGULUM

The data presented so far may well be interpreted as indicating that cream is incipient coagulum. The same factor which most frequently causes the formation of coagulum during polymerization—the absence of sufficient soap relative to the total surface area of the latex particles—appears to be responsible

for cream formation. However, the problem remains: what factors determine whether cream or coagulum will form in a given polymerization?

In order to vary the severity of the conditions of instability, a series of polymerizations was carried out in which the amount of electrolyte charged was varied. The quantity of potassium pyrophosphate in the recipe was held constant at the usual level, 0.25 part per 100 parts of charged monomers, while the potassium sulfate was varied between 0 and 1.0 part (0.4 part of potassium sulfate is ordinarily used). No stabilizing soap was added during these polymerizations. As shown by the data in Table VI, a considerable amount of coagulum formed when the potassium sulfate was reduced from the usual 0.4 part to 0.3 part or less. With 0.4 part or more present, large particles replaced nearly all of the coagulum; as the level of electrolyte was increased above 0.4 part, the percentage of large particles decreased and was very small when the potassium sulfate concentration reached 1.0 part. However, the elimination of large particles at high levels of electrolyte may possibly be due to the lowered final conversion. Thus, coagulum can be caused to form in place of cream by reduc-

TABLE VI
VARIATION IN AMOUNT OF POTASSIUM SULFATE IN UNSTABILIZED J-2820
TYPE LATEXES MADE WITH 70 PARTS OF WATER

No.	Potassium sulfate charged ^a (part)	Final conversion of monomers (%) ^b	Coagulum in unstripped latexes (%) ^c	Wt.-% between 20,000 and 100,000 Å in diameter ^{c,d}	Wt.-% over 100,000 Å in diameter ^{c,d}	Total wt.-% over 20,000 Å in diameter
1	0	83	40	0.7	0.3	1.0
2	0.1	77	34	0	0.8	0.8
3	0.2	76	20	0	10.6	10.6
4	0.3	69	0.4	33.8	4.6	38.4
5	0.4	65	1.3	31.5	0.4	31.9
6	0.6	55	0.2	14.8	0	14.8
7	0.8	38	0.3	1.8	0	1.8
8	1.0	37	0.3	2.6	0	2.6

^a Per 100 parts charged monomers.

^b Including monomers converted to coagulum.

^c Percentage based on total of latex polymer plus coagulum.

^d Mean of duplicate results on stripped latexes. Less than 1% additional coagulum formed on stripping.

ing the amount of electrolyte present, thereby increasing the severity of the conditions of instability. Both coagulum and cream were formed in the latex made with 0.3 part of potassium sulfate. This might be considered as an intermediate condition of instability. The large particles in this latex were over 100,000 Å in diameter, while the large particles in latexes made with more electrolyte were mainly between 20,000 and 100,000 Å in diameter. An interesting way of looking at the data is to consider coagulum as extremely large particles. As the electrolyte content is increased, the size of the large particles decreases from coagulum to particles larger than 100,000 Å, then to particles between 20,000 and 100,000 Å in diameter.

As the total amount of polymer produced increased with decreasing electrolyte concentration, it might be argued that the coagulum forms late in the polymerization. Therefore, it might form to a greater extent when less electrolyte is used because of the higher conversion, rather than because of the increase in the severity of the condition of instability. To check this possibility a series of polymerizations was carried to various conversions in the absence of potassium sulfate. The highest percentage conversion attainable before coagulum formed was less than 35 per cent, indicating that the formation of coagulum

owing to the reduction in electrolyte content was not caused by the increased extent of conversion of monomers.

Because cream is usually associated with the cold, high-solids type of latex, i.e., with relatively small amounts of water in the charge recipe, it was of interest to see whether coagulum formation could be induced in unstabilized J-2820 latex by an increase of the amount of water present. The effect of variation of the water content is shown in Table VII. It is apparent that when 90 parts or more of water are present, considerable quantities of coagulum form in preference to large dispersible particles. When 85 parts are present, both the large particles and prefloc are found, while less than 85 parts result essentially in the elimination of prefloc, which is replaced by the large particles. The slow reaction rate in the presence of 60 parts of water makes comparison with the other data difficult. It is noteworthy that the uncoagulated large particles are mainly over 100,000 Å in diameter when 85 parts of water are used, and between 20,000 and 100,000 Å in diameter when less water is present. Thus the size of agglom-

TABLE VII
VARIATION OF AMOUNT OF WATER IN UNSTABILIZED
J-2820 TYPE LATEXES

No.	Water charged ^a (parts)	Final conversion of monomers (%) ^b	Coagulum in unstripped latexes (%) ^b	Wt.-% between 20,000 and 100,000 Å in diameter ^{b,c}	Wt.-% over 100,000 Å in diameter ^{b,c}	Total coagulum plus particles over 20,000 Å in diameter (%)
1	60	36	0.6	0.9	0	1.5
2	70	61	1.1	24.1	6.0	31.2
3	75	68	0.9	31.8	4.6	37.3
4	80	71	1.6	26.4	5.6	34.6
5	85	82	14.1	2.6	12.0	28.7
6	90	83	36	0	1.5	37.5
7	95	89	38	0.3	0.8	39.1
8	100	98	38	0	0	38.0
9	110	101	38	0.6	1.4	40.0
10	120	103	37	0	1.5	38.5
11	130	103	36	1.6	1.2	38.8
12	140	102	28	0	0.4	28.4

^a Per 100 parts charged monomers.

^b Based on total polymer formed, including coagulum. Less than 2% additional coagulum formed in each case on stripping.

^c Mean of duplicate results on stripped latexes.

erates decreases from coagulum to particles over 100,000 Å in diameter, and then to particles between 20,000 and 100,000 Å; in this case, as the water level is gradually decreased. Increasing the amount of water, therefore, may be considered a means of increasing the severity of the condition of instability, which in turn results in larger agglomerates. However, the total percentage by weight of coagulum plus large particles (last column, Table VII) does not increase markedly with increasing amounts of water. Therefore, the presence of more water appears to favor a higher degree of agglomeration of a given number of particles, rather than an increase of the number of particles which undergo agglomeration to diameters larger than 20,000 Å.

To determine whether the higher conversions attained, when higher amounts of water were used, were responsible for the coagulum formation, a series of polymerizations was carried out in which the degree of conversion of monomers was varied in J-2820 latex made with 100 parts of water in the recipe. This was done by varying the time of reaction before shortstopping. The highest conversion attainable, before considerable amounts of prefloc formed, was only 31

percent. This showed that coagulum formation in the presence of increased amounts of water is not caused by the higher percentage conversion of monomers.

Because an increase of the amount of water charged, without a corresponding increase in electrolyte content, obviously results in a decrease of the electrolyte concentration, it was considered desirable to determine whether the formation of cream, rather than coagulum, in the presence of more water could be induced by a suitable adjustment in the amount of electrolyte. The results of a series of experiments in which the amount of electrolyte was varied in unstabilized J-2820 type latexes made with 100 parts of water (compared with the usual 70 parts) are shown in Table VIII. As was found in the experiments in which 70 parts of water were present (Table VI), it is evident that coagulum is replaced by large particles when a sufficiently high concentration of electrolyte is used in the presence of 100 parts of water. However, a minimum of 1.0 part of electrolyte was required in this case, as compared with 0.4 part when 70 parts of water were used. Electrolyte concentrations cannot be directly com-

TABLE VIII
VARIATION OF AMOUNT OF POTASSIUM SULFATE IN UNSTABILIZED J-2820
TYPE LATEXES MADE WITH 100 PARTS OF WATER

No.	Potassium sulfate charged ^a (parts)	Final conversion monomers (%) ^b	Coagulum in unstripped latexes, (%) ^b	Additional coagulum formed on stripping (%) ^b	Wt.-% between 20,000 and 100,000 Å in diameter ^{b,c}	Wt.-% over 100,000 Å in diameter ^{b,c}
1	0	91	11	11	1.1	3.1
2	0.4	93	28	0.4	0	4.1
3	0.6	82	32	0.4	0.2	2.4
4	0.7	87	28	1.0	1.4	2.7
5	0.8	66	25	0.4	5.2	2.9
6	0.9	64	24	0.4	1.5	9.2
7	1.0	63	0.4	0.9	5.4	27.6
8	1.1	73	0.1	0.5	24.1	19.6
9	1.2	65	0.1	0.5	28.8	17.8
10	1.3	72	0.0	0.6	26.2	12.5
11	1.4	65	0.1	0.8	20.2	11.1
12	1.5	67	0.2	0.9	22.0	9.4

^a Per 100 parts charged monomers.

^b Based on total polymer formed, including coagulum.

^c Mean of duplicate results on stripped latexes.

pared because 0.25 part of potassium pyrophosphate was present in each series, and its effectiveness relative to that of potassium sulfate is not accurately known. It appears that electrolyte concentration determines whether cream or coagulum will form at a given water level, as a higher amount of electrolyte prevents coagulum from forming when the amount of water is increased. It is also apparent from Table VIII that when 0.8 or 0.9 part of potassium sulfate is used, appreciable amounts of both coagulum and large particles are formed. At these intermediate levels of electrolyte, the large particles are mainly over 100,000 Å in diameter, whereas most of the weight of large particles appears in the range 20,000 to 100,000 Å when more electrolyte is present. Thus once again a decrease of the size of agglomerates is observed as the condition of instability is made less severe.

EFFECT OF CROSS-LINKING IN POLYMER ON FORMATION OF CREAM AND COAGULUM

The attempt to remove the modifier (*tert*-dodecanethiol) from J-2820 latex in large-scale polymerizations, and thus produce a latex containing a polymer of

high molecular weight, results in the formation of coagulum. Because this latex ordinarily contains some cream, it appeared conceivable that the unmodified latex might tend to agglomerate more completely, for some unknown reason, than the same type of latex containing polymer of lower molecular weight, as made in the presence of modifier. In view of this, an investigation of the mechanism of destabilization in the absence of modifier appeared to be of considerable interest.

To determine the effect of modifier concentration on the formation of large particles and coagulum, a series of polymerizations was carried out in which the modifier concentration was varied between 0 and 0.16 part per 100 of monomers, in J-2820 latex. (Normally 0.10 part of modifier is present.) No stabilizer was added during these polymerizations. The results recorded in Table IX show that almost 5 per cent by weight of coagulum forms when the modifier is omitted from the formula. A smaller amount of coagulum forms when 0.01 part of modifier is present, and 0.02 part or more reduces the amount of coagu-

TABLE IX
VARIATION OF AMOUNT OF MODIFIER IN UNSTABILIZED
J-2820 TYPE LATEXES

No.	tert-Dodecanethiol (part ^a)	Final conversion of monomers (%) ^b	Coagulum in unstripped latexes (%) ^b	Wt.-% of particles over 20,000 Å in diameter ^{b,c}
1	0	61	4.9	23.5
2	0.01	62	1.6	32.4
3	0.02	62	0.5	35.8
4	0.03	63	0.2	44.1
5	0.04	60	0.4	28.6
6	0.05	60	0.03	29.6
7	0.06	58	0.5	35.6
8	0.08	63	0.2	36.9
9	0.10	59	0.08	35.4
10	0.12	59	0.05	34.1
11	0.14	57	0.05	42.2
12	0.16	64	0.2	37.7

^a Per 100 parts charged monomers.

^b Based on total polymer formed, including coagulum. Less than 1% additional coagulum formed on stripping these latexes.

^c Mean of duplicate results on stripped latexes.

lum to a small value. The data on weight percentage of particles over 20,000 Å in diameter, given in the last column of Table IX, indicate that the formation of coagulum in the absence of modifier occurs at the expense of very large particles, since there is a decrease in the percentage of such particles when modifier is omitted. One may best interpret these data by assuming that the absence of modifier influences the mechanism of agglomeration in such a way that it tends to continue until some coagulum is formed. The fact that only part of the large particles are replaced by coagulum does not conflict with the observation that some modifier must be used in large-scale production of this type of latex, since tolerances for coagulum are very small, compared with cream.

Omission of modifier results in a crosslinked polymer of high molecular weight. In order to study further the effect of cross-linking on the mechanism of agglomeration a series of J-2820 type latexes was prepared in which varying amounts of a cross-linking agent divinylbenzene were present in the polymerization recipe. No stabilizing soap was added during the polymerization in these experiments. In the first half of Table X results are recorded which

were obtained with the use of the usual amount of potassium sulfate 0.4 part, in the charge recipe. Data in the second half of the table correspond to the use of 0.6 part of potassium sulfate. In each case little coagulum, but large amounts of giant particles, were present in the latexes made without divinylbenzene. However, with 0.4 part of electrolyte present, the use of 1 part of divinylbenzene resulted in the formation of appreciable amounts of coagulum, while large quantities of coagulum were present when 3 parts or more of divinylbenzene were used. As was found earlier, in reducing the modifier content, the formation of coagulum was accompanied by a decrease of the amount of dispersible large particles, thus giving further evidence that a highly cross-linked polymer tends to continue agglomerating until coagulum is formed.

In a separate series of experiments it was found that 97.5 per cent of the polymer made on the J-2820 recipe was soluble in benzene; however, the presence of only 0.1 part of divinylbenzene in the charge recipe caused the formation of 61 per cent gel (insoluble polymer) and, as might then be expected, the pres-

TABLE X
VARIATION OF AMOUNT OF DIVINYLBENZENE ADDED TO
UNSTABILIZED J-2820 TYPE LATEXES

No.	Divinylbenzene charged ^a (parts)	Potassium sulfate charged ^a (parts)	Final conversion of monomers (%)	Coagulum in unstripped latexes (%)	Additional coagulum formed on stripping (%)	Wt.-% between 20,000 A and 100,000 A in diameter ^{b,c}	Wt.-% over 100,000 A in diameter ^{b,c}	Total coagulum plus particles over 20,000 A in diameter (%)
1	0.0	0.4	61	1.1	0.3	24.8	13.6	39.8
2	0.1	0.4	59	0.6	1.0	11.3	24.4	37.3
3	0.5	0.4	50	0.9	0.5	15.0	22.5	38.9
4	1.0	0.4	59	1.0	5.0	17.8	15.7	39.5
5	3.0	0.4	68	19.0	13.0	2.4	4.6	39.0
6	5.0	0.4	76	28	1.8	11.4	3.4	44.6
7	0.0	0.6	56	0.2	0.4	28.2	7.1	35.9
8	0.1	0.6	52	0.6	0.2	36.4	5.0	42.2
9	0.5	0.6	53	0.4	0.5	37.6	2.7	41.2
10	1.0	0.6	56	1.3	0.8	29.6	8.7	40.4
11	3.0	0.6	58	13.0	8.4	8.4	11.4	41.2
12	5.0	0.6	60	26	6.4	11.7	1.5	45.6

^a Per 100 parts charged monomers.

^b Based on total polymer formed, including coagulum.

^c Mean of duplicate results on stripped latexes.

ence of 1 part of divinylbenzene resulted in the formation of a polymer that was almost completely insoluble (95 per cent gel). Thus, the polymer must be tightly cross-linked if an appreciable replacement of cream by prefloc is to occur.

It does not appear that the major effect of cross-linking is to cause more of the small original particles to agglomerate; there is some increase of the total of large particles plus coagulum when 5 parts of divinylbenzene are present, but most of the coagulum formation shown in Table X is accompanied by a corresponding decrease of the amount of dispersible, large particles. One may conclude, therefore, that the over-all instability is not greatly affected by cross-linking of the polymer. The important effect appears to be on the mechanism of agglomeration. This conclusion is given additional support by the experiments discussed next.

To look further into the mechanism of agglomeration of latex particles containing cross-linked polymer, another series of experiments was performed based on the use of divinylbenzene. Increasing amounts of rosin soap were substituted for part of the mixed soap in unstabilized J-2820 type latexes containing divinylbenzene. The experiments were similar to those summarized in

Table V, except that 3 parts of divinylbenzene were present in each bottle. The effects of substituting rosin soap for mixed soap on a 3 to 1, or a 4 to 1, basis by weight are shown in Table XI. As expected, large amounts of both dispersible giant particles and coagulum formed when only the mixed soap was used. As increasing amounts of rosin soap were substituted, i.e., as the total amount of soap present increased, the amount of agglomerates decreased, and was small when the total soap content exceeded 2.8 to 3 parts. These results are very similar to those obtained without the use of divinylbenzene (Table V), except that prefloc formed in place of some of the cream when insufficient rosin soap was present. The amount of rosin soap needed to prevent the formation of large agglomerates was nearly the same whether or not divinylbenzene was present. However, in the presence of the cross-linking agent, the formation of very large agglomerates (coagulum) was favored.

TABLE XI
SUBSTITUTION OF ROSIN SOAP^a FOR MIXED SOAP^b IN UNSTABILIZED
J-2820 TYPE LATEXES MADE WITH 3 PARTS OF DIVINYLBENZENE^c

	No.	Mixed soap charged ^d (parts)	Rosin soap charged ^e (parts)	Final conver- sion of monomers (% ^f)	Coagulum in un- stripped latexes (% ^{g,h})	Wt.-% between 20,000 and 100,000 Å in diameter ^{d,f}	Wt.-% over 100,000 Å in diameter ^{d,f}
A. Substitution on 3 to 1 basis	1	1.25	0.0	70	22	16.3	7.3
	2	1.05	0.6	69	26	6.9	0.5
	3	0.85	1.2	69	17	9.0	9.5
	4	0.65	1.8	57	8	0.0	1.5
	5	0.45	2.4	58	1	3.2	1.6
	6	0.25	3.0	58	1	1.8	3.5
	7	0.0	3.75	78	1	0.0	1.0
B. Substitution on 4 to 1 basis	1	1.25	0	70	22	16.3	7.3
	2	1.05	0.8	76	19	8.0	7.5
	3	0.85	1.6	57	6	2.0	2.5
	4	0.65	2.4	50	2	1.6	0.0
	5	0.25	4.0	71	1	4.0	0.0

^a For chemical description see Table V.

^b For chemical description see Table I.

^c Per 100 parts charged monomers.

^d Based on total polymer formed, including coagulum.

^e Less than 1% additional coagulum formed on stripping.

^f Mean of duplicate results on stripped latexes.

These data give additional support to the hypothesis that the effect of cross-linking in the polymer is to alter the mechanism of agglomeration in some manner so as to prevent it from stopping at the stage where the particles are large, but dispersible. About the same percentage of the polymers appears as agglomerates when cross-linking is introduced, and no increased difficulty is encountered in attempting to produce a stable latex by suitable choice of soap, but the formation of larger agglomerates is favored. Although no definite conclusion can be drawn as to the effect of cross-linking, one possibility is that the difference in mechanism of agglomeration is related to the fact that a cross-linked polymer is less cohesive than a linear polymer of the same type, and that cohesion is related to the ability of particles to fuse into larger spherical particles.

To determine whether a general increase in particle size is associated with the formation of cream, in each of the ten experiments represented in Figure 2, the average particle size of the latex after removal of cream, was determined in the spectrophotometer⁴. In the first experiment, in which no stabilizing soap was added, the average particle diameter was 1850 Å. In the other nine experiments, the average particle size varied within a narrow range of diameters, 1480

to 1640 Å, and showed no trend with increasing stabilizer. The consistency of this average diameter indicates that agglomeration, once started, tends to continue until extremely large particles are formed; any appreciable quantity of particles of intermediate size would have resulted in marked increases of the average diameter, as obtained by measurement of turbidity, which weights large particles heavily.

SUMMARY

The formation of cream, which occurred in many of the early cold, high-solids GR-S latexes, is undesirable because it results in nonuniformity of the latex and is injurious to the properties of latex films. On the other hand, it is dispersible and, hence, much more tolerable than coagulum. The mechanism of its formation is, therefore, of interest. A cold high-solids latex activated by ferrous sulfide was used as the basis for the study.

The giant particles constituting cream begin forming between 18 and 35 per cent conversion in latex stabilized only with the soap present initially, and increase in quantity until the end of polymerization. Their formation can be prevented by the timely addition of sufficient stabilizing soap, or by the use of a soap which initiates a small enough number of particles in relation to its stabilizing capacity. The formation of coagulum, rather than large particles, is favored by decreasing the amount of electrolyte or increasing the amount of water charged, and by the presence of cross-linking in the polymer. The effect of increasing the water level or introducing cross-linking is to increase the size rather than the amount of agglomerates.

Methods are suggested for controlling the formation of very large particles.

ACKNOWLEDGMENT

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WATER-SOLUBLE ACIDS OF THE LATEX OF HEVEA BRASILIENSIS *

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The composition of the latex of *Hevea brasiliensis* has been the subject of numerous investigations, and an extensive list of compounds, other than rubber, has been reported to be present. Some of these have been assumed on the basis of qualitative tests, and their existence in latex is doubtful. The known organic nonrubber components present in highest quantity in ammonia-preserved latex are protein, protein fragments, and quebrachitol.¹ The plant acids, commonly present in plant sera, are noticeably absent from the list of identified materials. Stewart, Bonner, and Hummer² have observed citric and malic acids in the latex of *Cryptostegia grandiflora*, and McCollm³ discovered citric acid in an aqueous extract of the bark of *Hevea brasiliensis*, but the only water soluble acids previously reported in *Hevea* latex have been identified in inadequately preserved latex, and are recognized as products of putrefaction⁴.

For many years, water-soluble acids have been assumed to be present in preserved latex, and their importance for stability and compounding⁵ has been recognized. Qualitative studies of the free acid concentration of a number of preserved latexes have been reported⁶ which indicate that the acid concentration is quite variable; fresh latex is relatively free of acids, which appear slowly when an alkaline preservative is used.

Rider⁷ isolated from latex a crude mixture which seemed to include the naturally occurring antioxidant material. Examination of this mixture by the author showed it to contain a small amount of an amino acid mixture (not further investigated) and a mixture of plant acids. Malic and citric acids were identified by qualitative tests. The yield of crude mixture from the latex suggested that these acids were present in relatively high concentrations in serum.

EXPERIMENTAL

To check this observation, two samples of *Hevea* latex serum were examined. The first⁸ was serum obtained during the preparation of a commercial creamed concentrated latex, preserved with about 2 per cent ammonia. The second was prepared from a commercial normal (unconcentrated) latex by centrifuging to give a serum of low rubber content. The analytical procedure was the same for both sera, and may be illustrated by the results for the first sample, on which the following preliminary analyses were made:

	Percentage by weight
Total solids	6.8
Acid coagulable	3.3
Rubber hydrocarbon	2.6
Ammonia	ca. 1.9
Non-ammonia nitrogen	0.22
Ash	0.41

* Reprinted from the *Rubber World*, Vol. 131, No. 1, pages 60-70, 75, October 1954.

Three-thousand grams of serum was stirred in a stream of air in a large evaporating dish at 90° C to remove ammonia. When the ammonia level had fallen to less than 0.1 per cent, a strong acid ion exchange resin (Dowex-50)⁹ was added to adjust the pH to 4.0 (53 grams) and the resulting coagulum was consolidated by standing a further half hour at 90° C. The slurry was filtered hot, and the clear serum, after cooling, was passed through a fully regenerated column of Dowex-50 to remove cations, then through a column of an anion exchanger (Amberlite-IR45)¹⁰ in the hydroxyl form, to recover acids. Effluent pH from the cation exchanger was 1.9; from the anion exchanger, 4.5. Passage through a second set of ion exchangers yielded a final effluent of pH 8.9, which, on concentration, gave 27 grams of crude quebrachitol, n.p. 179–181° C.

The effluent from the cation exchanger contained 262 milliequivalents of free acid, of which 242 were recovered from the anion exchangers by elution with dilute ammonia. Two hundred milliequivalents were separated into fractions on a column of strong-base anion exchanger (Dowex-2) by elution with ammonium carbonate. The resin, in a column 45 by 400 millimeters, was treated with 5 per cent ammonium carbonate till free of chloride, then was washed with distilled water. The solution of ammonium salts of the serum acids was passed through the column slowly, followed by a water wash. The column was eluted with a series of solutions of ammonium carbonate of increasing concentration; monobasic acids were completely removed by a 0.5 per cent solution, dibasic by 1.5 per cent and tribasic by 3 per cent. The separation was followed by collecting eluate in 100-milliliter fractions and titrating aliquots at regular intervals, after removal of carbonate and excess ammonia.

RESULTS

The results are plotted in Figure 1, in which the peaks corresponding to known acids are identified. The relative positions of phosphate, sulfate, malate, and citrate on the chromatogram were determined by model experiments with mixtures of known acids, and the identifications verified by direct analysis of appropriate fractions from the unknown mixture for phosphorus and sulfur and by assay of the major peaks for malate and citrate.

Concentration of the solutions containing the acids appearing as the first peak (PCA) in Figure 1 yielded a syrup. This syrup gave color reactions, with phenols in concentrated sulfuric acid, similar to those given by alginic acid, the creaming agent used in the serum preparation. This high molecular-weight acid, however, is not readily adsorbed by exchange resins. Repetition of the separation with the second serum, which contained no added alginate, gave a similar peak. Fractionation of a portion of this material, by a modification of the procedure of Marvel and Rands¹¹, showed that the major component was a crystalline acid [m.p. 158° C (uncorrected), neutral equivalent 130, per cent nitrogen 10.55]. The properties suggested that it was pyrrolidone carboxylic acid, formed from glutamic acid during the processing of the serum in preparation for recovery of the acid fraction. Its identity was verified by comparison of an x-ray diffraction pattern with that of an authentic specimen. [No glutamic, or aspartic, acid was isolated from the mixture of acids recovered from the anion exchanger. Both of these were identified in the cation exchanger eluate: glutamic acid (0.024 per cent of the serum) as the hydrochloride and aspartic acid (0.018 per cent of the serum) as the copper salt.]

At least two other acids, not yet identified, occur in this pyrrolidone carboxylic acid fraction. Paper chromatography in several solvent combinations

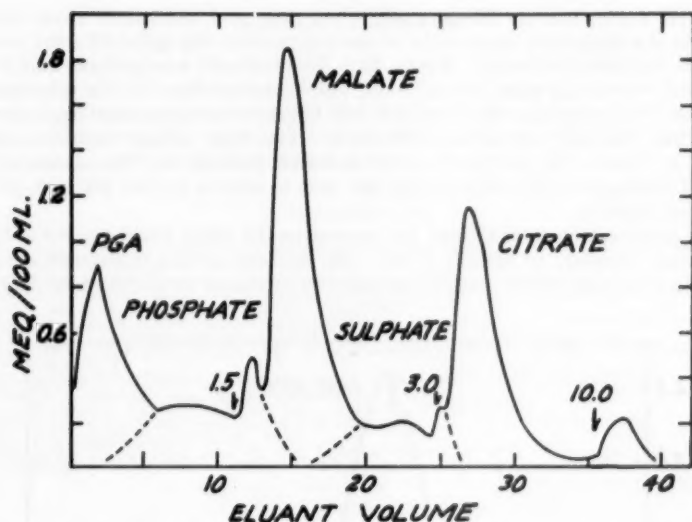


FIG. 1.—Fractionation of Hevea cream serum acids. Initial ammonium carbonate concentration 0.5%; concentrations changed after each major peak as indicated by arrows. Overlapping of sulfate and phosphate into adjacent peaks is shown by dashed lines. Abscissa units arbitrary: Figures 1 and 2 adjusted to be comparable.

showed the presence of two phosphorus-containing acids in addition to the pyrrolidone carboxylate.

A material balance for this separation shows that about 80 per cent (equivalent) of the acids was identified and about 10 per cent was strongly adsorbed on the column:

Peak (Figure 1)	Acid	Milliequivalents found
1	Pyrrolidone carboxylic	31.8
2	Phosphoric	21.0
3	Malic	60.0
4	Sulfuric	12.0
5	Citric	38.4
6	Unknown	5.2
—	Washed through	9.2
—	Left on column	21.4
	Total taken	199.6

The compositions of the acid mixtures isolated from the two different sera were quite similar, except that the phosphorus-containing fraction was much larger in the normal latex serum. This latex came from Sumatra; the cream serum from Malaya. Sumatran latexes have been found frequently to have higher phosphorus content than Malayan.

The identified plant acids were estimated to constitute about 0.35 per cent (by weight) of the aqueous phase of the cream serum and about 0.5 per cent of the centrifuged latex serum, which were both at least one year old when used. In contrast to this point, Rider⁷ reported that no acid fraction was isolated from a sample of freshly ammoniated serum worked up the day after preservation.

A sample approximately 20 days old, when processed, contained about 0.05 per cent of a mixture of plant acids, whose composition was quite different from the two examined previously (Figure 2). No citric acid was present, and the first peak was nearly pure succinic acid, which was not found in the other two samples. The succinic acid [m.p. 184–185° C (uncorrected) neutral equivalent 60.0] was identified by x-ray diffraction. The high sulfate concentration shown in Figure 2 is the result of the isolation procedure. The serum was treated alternately with sulfuric acid and lime to remove rubber, fat acid, protein, and alginate.

No study of the method used for separating the plant acids was made beyond that necessary to identify them. On the basis of this experience, it appears to be a convenient method for analysis of simple mixtures or for large-

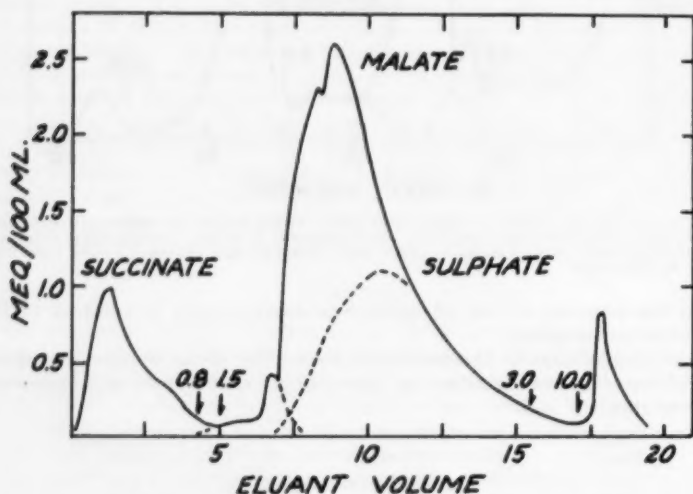


FIG. 2.—Fractionation of acid mixture from 20-day-old latex. Ammonium carbonate concentrations as indicated.

scale preparative work (in one experiment a column was loaded to 90 per cent of its capacity with mixed serum acids, and a satisfactory separation obtained). While this work was in progress, Bryant and Overell¹² reported the qualitative application of the same procedure on a small scale to separate di- and tribasic acid fractions before paper chromatography. More recently, several workers¹³ have described analytical procedures for the separation of mixtures of plant acids, using a strong base exchange resin.

SUMMARY

Malic, citric, and succinic acids have been identified as components of the serum of *Hevea brasiliensis* latex preserved with ammonia. It has been confirmed that the plant acids are present in low concentrations in fresh latex but form a large fraction of the water-soluble serum solids.

ACKNOWLEDGMENTS

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NONRUBBER COMPONENTS OF AMMONIA-PRESERVED LATEX. AN ANALYTICAL STUDY *

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INTRODUCTION

The analysis of the nonrubber components of latex has been the subject of intensive study for many years, and includes general schemes of separation¹ and the determination of particular components, such as phospholipin², proteins and amino acids³, nitrogen compounds⁴ and acids⁵. Changes in the composition of nonrubber components have also been followed⁶, as have changes in the latex structure brought about by the nonrubber⁷ components.

However, despite a general picture of the latex system being already available, the many changes occurring in ammoniated latex make it impossible to assess in more than a general way its composition at the time when it is to be processed, usually about three months after tapping. Nor is it possible to assess what differences are likely to be encountered between consignments of ammoniated concentrate. For these reasons, latex analysis was undertaken in this country. The composition of the nonrubber components at the time of processing is considered. A study of ammoniated concentrate, field latex, and serum has been used to obtain the distribution of nonrubber components between the serum and rubber/serum interface.

ISOLATION AND COMPOSITION OF NONRUBBER COMPONENTS

A number of methods for the isolation of the nonrubber components were compared, including the solvent extraction of the dry film and aqueous extraction of a rubber solution. Experiments were also carried out by the method of Dekker⁸, in which the rubber is dissolved in xylene and extracted with dilute acetic acid, and by that of Altman⁹. The last method was finally adopted; it consists of alcohol coagulation of the latex, followed first by alcohol extraction, then by water extraction of the coagulum. The percentage of alcohol-soluble material obtained by this method is constant within narrow limits; the water extract following is less constant, but is small in amount. The main protein of the latex remains with the rubber, and may be estimated by the nitrogen content of the coagulum.

The nonrubber components are divided into ether-soluble and ether-insoluble portions. The classification made by Baker⁵ of ether-solubles as rubber interface material was confirmed by the very low ether-soluble content (0.06 per cent) of electrodecented serum containing about 1 per cent of rubber; however, it is possible that those ammonium salts which dry down to free ether-soluble acids may come from the serum.

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ETHER-SOLUBLE COMPONENTS

The ether-soluble material from a centrifuged concentrate contains a considerable amount of free acid, amounting to about 1 per cent of the dry rubber weight, thus confirming the finding of Baker⁵. The average equivalent of the acid is about 360, and the iodine value of the acid fraction shows it to be slightly more unsaturated than oleic acid, as found by Roberts¹⁰ and Baker⁵. Potentiometric titration of the ether-soluble acids with alcoholic potash shows equivalence points at pH 9.6-9.7, and the shape of the curves is in each case that of a weak acid in an unbuffered system. The ether-soluble acids are known to be formed by phospholipin hydrolysis¹¹, and the absence of ether-soluble phosphorus in the alcohol extract confirms that phospholipin hydrolysis has taken place, with consequent removal of phosphorus into the aqueous phase.

The nonacid part of the ether-solubles contains saponifiable material, and may be separated from ether-soluble acids by acetone extraction of a film made from latex to which an excess of soda has been added, followed by ether extraction of the dry acetone extract. Saponification of this fraction, either with alcoholic potash or with the anion-exchange resin Deacidite-FF, gives sterol and acid components. Removal of the acid component from its alcoholic solution

TABLE 1

TYPICAL ANALYSIS OF ETHER-SOLUBLE MATERIAL IN AN AMMONIATED LATEX CONCENTRATE

Total ether-solubles	2.1 per cent
Non-acid fraction	1.2 per cent
Acid fraction	0.9 per cent
Acid value	1.1 mg. KOH/g. latex
Saponification value	0.7 mg. KOH/g. latex
Sterol	0.9 per cent

The above percentages are based on total solids weight.

on the anion-exchange resin leaves a white solid, melting point 130° C; qualitative tests indicate that it is a sterol. The acid component was first separated by eluting from the anion-exchange resin with phosphoric acid. The eluate was then steam-distilled under controlled conditions and gave a distillation curve characteristic of acetic acid. The saponifiable material is, therefore, identified as a phytosterol acetate. The sterol ester content of an electrodecanated concentrate, a centrifuged concentrate and a skim crepe differ only slightly, so this component may be classified as a part of the rubber phase itself, rather than interface material.

Quantitative data on ether-solubles are summarized in Table 1.

WATER-SOLUBLE MATERIAL

The ether-insoluble portion of the nonrubber components is, in general, soluble in water and will be referred to as "water-solubles". Qualitative tests reveal the presence in the water-solubles of choline and some free phosphate. When hot alcohol is used for the initial coagulation, the alcohol extract still contains choline; the presence of this substance is, therefore, not due to its enzymic formation on coagulation, described by Smith¹². The amount of free phosphate is considerably increased by acid hydrolysis or by alkaline ashing of the water-solubles, suggesting that the phosphate is mainly in a combined form; it is probably glycerophosphate, which behaves similarly. These findings con-

firm that phospholipin hydrolysis has taken place. The presence of these same phospholipin hydrolysis products in electrodecanated serum containing about 1 per cent of rubber shows that the hydrolysis has commenced at the time when the latex was concentrated; the extent of the hydrolysis is considered later.

The total water-solubles give an acidic solution; a pH titration curve indicates a well-buffered system, with the sharpest change between pH 7.5 and pH 8.3. The acidic components of the water-solubles have been isolated by the use of ion-exchange resins. A very dilute solution of the water-solubles is passed through the cation-exchangers Zeokarb-215 or Amberlite-IR-112H, then through the anion-exchanger Deacidite-FF. The acids absorbed on the anion-exchanger are progressively removed with acetic acid, followed by hydrochloric acid. The stronger acid fraction, containing phosphoric acid, amounts to 0.3 to 0.4 per cent of the serum weight, and has an average equivalent of about 120. A similar amount of unidentified weakly acid material is eluted with acetic acid. Using the method of Lugg and Overell¹³, Patrick¹⁴ has shown by chromatographic means the presence in latex of oxalic, tartaric, citric, malic, malonic, succinic, fumaric, oxaloacetic, glyoxylic, pyruvic, and α -ketoglutaric acids; it is evident that the acid radicals in latex are complex in nature. The latex also contains volatile acid which are not retained in the water-solubles by the method of isolation used. They are determined by steam distillation of acidified latex serum in the presence of phosphoric acid, a modification of the method of Philpott¹⁵. The volatile acids are mainly formic and acetic acids, with a small amount of higher fatty acids, and they are found in latex in widely differing amounts. Properly prepared bulk shipments have been found to contain the smallest quantities, which agrees with Philpott's view that volatile acids give a measure of the degree of putrefactive degradation of the latex.

Titration with and without formaldehyde to pH 9.5 gives an indication of the amino acid content of the water-solubles, assuming that the sequestered amino groups are equivalent to the carboxyl groups. The amino-acid content of the water-solubles is quite small, of the order of 0.1 per cent for serum. Amino acids and choline together do not account for the total nitrogen content of the water-solubles, suggesting that there are also compounds intermediate in molecular weight between amino acids and the precipitated proteins. The behavior of the water-solubles with ion-exchange resins confirms the existence of such molecules. Cation-exchangers leave a part of the water-soluble nitrogenous material unabsorbed, the amount depending on the pore size of the resin. The resins will, however, remove amino acids, even if acidic as in the case of aspartic acid, or of relatively high molecular weight, as in the case of tyrosine. The Rubber Research Institute of Malaya reports¹⁶ that polypeptide fractions are not present in fresh latex, so the residual nitrogen compounds are either alcohol-soluble proteoses and peptones or hydrolytic breakdown products of proteins.

The metal content of the water-solubles is sometimes less than the equivalent of the total acid content, and this suggests the presence in ammoniated latex of some acids in the form of their ammonium salts. If the acids are of a strength comparable with acetic or citric acid, the ammonium salts may be detected by nitrogen determinations on the dried films made from the latex with and without the addition of soda. The difference represents undecomposed ammonium salts, since ammonium acetate and citrate normally retain their ammonia in the film, unlike ammonium salts of weaker acids, such as oleic acid and alanine, which dry down in the film to the free acid. Ammonium salts are found in some, but not all, latex samples; the amount increases with the

age of the latex at a rate which varies from sample to sample. These ammonium salts will be included in the KOH number of the latex. Van den Tempel¹⁷, in evaluating the components of the KOH number, finds in some cases a difference between the acids determined and the KOH number; these ammonium salts probably account for the difference as he suggests.

A large proportion of the water-solubles consists of carbohydrate material, mainly quebrachitol; the amount was found to vary considerably between a seedling latex and latex from clone G.1. The carbohydrate fraction is isolated from other components by passage of the water-solubles successively through strongly acidic and basic ion exchangers. It crystallizes readily, the recrystallized compound melting at 181° C. The optical rotation of the fraction is consistent with its containing 90 per cent of quebrachitol. The whole fraction reduces ammoniacal silver nitrate, but not Fehling's solution, indicating the virtual absence of free reducing sugars. It is also practically free of phosphorus. Quebrachitol is removed from a rubber film by acetone extraction and is the main component of the ether-insoluble part of the acetone extract of a film from soda-treated latex.

The mineral content of rubber latex, judged from the ash, consists mainly of potassium salts; it also contains a small and variable amount of magnesium and traces of copper, iron, and manganese. Other metals have not been investigated. The ash contains a small amount of sulfate, but consists mainly of phosphate and carbonate. The low figure of 0.05 per cent obtained for the soap remaining after removal of ammonium soap shows that potassium is not in the latex as a soap, but is combined with stronger acids, including phosphoric acid, and probably the organic acids mentioned earlier in this section. The latter salts would give rise to the potassium carbonate in the ash. The present findings with regard to mineral components are in agreement with those of Beadle and Stevens¹⁸, Flint¹⁹ and others who have taken the investigation further and shown the presence of sodium, rubidium and calcium.

PROTEIN

The nature of the protein in rubber latex has not been investigated here. The amount of protein has been found from the nitrogen content of the alcohol- and water-extracted coagulum; probably proteoses and peptones remain uncoagulated by this procedure. Corresponding determinations on centrifuged skim and serum remaining after electrodecentration suggest that the aqueous phase contains protein not adsorbed on the rubber particles at the time of concentrating.

The extracted rubber coagulum contains a small amount of phosphorus. After repeated diluting and centrifuging, after coagulation by freezing and even after soap addition, residual nitrogen and phosphorus were found on the rubber. It seems likely, therefore, that latex contains phosphoprotein. This agrees with the findings of Sekhar and McMullen²⁰ that the protein fractions which they isolated from latex contain phosphorus. The ratio of coagulum or rubber phase nitrogen to phosphorus remains approximately constant for latex concentrates, but this nitrogen/phosphorus ratio rises by a factor of about eight for skim or serum. It seems, therefore, that in the serum there are proteins containing no phosphorus and that the phosphoproteins are located at the rubber/serum interface.

The figures obtained in the course of a typical analysis of a latex concentrate are given in Table 2. They are based on total solids weight.

firm that phospholipin hydrolysis has taken place. The presence of these same phospholipin hydrolysis products in electrodecented serum containing about 1 per cent of rubber shows that the hydrolysis has commenced at the time when the latex was concentrated; the extent of the hydrolysis is considered later.

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The metal content of the water-solubles is sometimes less than the equivalent of the total acid content, and this suggests the presence in ammoniated latex of some acids in the form of their ammonium salts. If the acids are of a strength comparable with acetic or citric acid, the ammonium salts may be detected by nitrogen determinations on the dried films made from the latex with and without the addition of soda. The difference represents undecomposed ammonium salts, since ammonium acetate and citrate normally retain their ammonia in the film, unlike ammonium salts of weaker acids, such as oleic acid and alanine, which dry down in the film to the free acid. Ammonium salts are found in some, but not all, latex samples; the amount increases with the

age of the latex at a rate which varies from sample to sample. These ammonium salts will be included in the KOH number of the latex. Van den Tempel¹⁷, in evaluating the components of the KOH number, finds in some cases a difference between the acids determined and the KOH number; these ammonium salts probably account for the difference as he suggests.

A large proportion of the water-solubles consists of carbohydrate material, mainly quebrachitol; the amount was found to vary considerably between a seedling latex and latex from clone G.1. The carbohydrate fraction is isolated from other components by passage of the water-solubles successively through strongly acidic and basic ion exchangers. It crystallizes readily, the recrystallized compound melting at 181° C. The optical rotation of the fraction is consistent with its containing 90 per cent of quebrachitol. The whole fraction reduces ammoniacal silver nitrate, but not Fehling's solution, indicating the virtual absence of free reducing sugars. It is also practically free of phosphorus. Quebrachitol is removed from a rubber film by acetone extraction and is the main component of the ether-insoluble part of the acetone extract of a film from soda-treated latex.

The mineral content of rubber latex, judged from the ash, consists mainly of potassium salts; it also contains a small and variable amount of magnesium and traces of copper, iron, and manganese. Other metals have not been investigated. The ash contains a small amount of sulfate, but consists mainly of phosphate and carbonate. The low figure of 0.05 per cent obtained for the soap remaining after removal of ammonium soap shows that potassium is not in the latex as a soap, but is combined with stronger acids, including phosphoric acid, and probably the organic acids mentioned earlier in this section. The latter salts would give rise to the potassium carbonate in the ash. The present findings with regard to mineral components are in agreement with those of Beadle and Stevens¹⁸, Flint¹⁹ and others who have taken the investigation further and shown the presence of sodium, rubidium and calcium.

PROTEIN

The nature of the protein in rubber latex has not been investigated here. The amount of protein has been found from the nitrogen content of the alcohol- and water-extracted coagulum; probably proteoses and peptones remain uncoagulated by this procedure. Corresponding determinations on centrifuged skim and serum remaining after electrodecantation suggest that the aqueous phase contains protein not adsorbed on the rubber particles at the time of concentrating.

The extracted rubber coagulum contains a small amount of phosphorus. After repeated diluting and centrifuging, after coagulation by freezing and even after soap addition, residual nitrogen and phosphorus were found on the rubber. It seems likely, therefore, that latex contains phosphoprotein. This agrees with the findings of Sekhar and McMullen²⁰ that the protein fractions which they isolated from latex contain phosphorus. The ratio of coagulum or rubber phase nitrogen to phosphorus remains approximately constant for latex concentrates, but this nitrogen/phosphorus ratio rises by a factor of about eight for skim or serum. It seems, therefore, that in the serum there are proteins containing no phosphorus and that the phosphoproteins are located at the rubber/serum interface.

The figures obtained in the course of a typical analysis of a latex concentrate are given in Table 2. They are based on total solids weight.

TABLE 2

WATER-SOLUBLE, PROTEIN, AND ASH CONTENT OF A
TYPICAL LATEX CONCENTRATE

	Per cent
Total water-solubles	2.63
Acetone-soluble, acidic water-solubles (held back by NaOH)	0.48
Acetone-soluble, nonacidic water-solubles (quebrachitol)	0.43
Water-soluble acids	0.91 mg. KOH/g. latex
Water-soluble nitrogen (expressed as protein)	0.69
Total ash	0.30
Total phosphorus	0.040
Magnesium in ash	0.003
Copper in ash	0.0003
Total nitrogen (expressed as protein)	1.12

TABLE 3

COMPARISON OF NONRUBBER COMPONENTS FROM ELECTRODECANTED AND
CENTRIFUGED CONCENTRATES

	Electro-decanted concentrate (per cent)	Centrifuged concentrate (per cent)
1. Total solids	62.6	63.3
2. Total alcohol- and water-solubles	5.06	4.39
3. Ether-solubles from 2	2.29	1.98
4. Water-solubles from 2	2.77	2.40
5. Acetone extract	3.66	2.80
6. Ether-solubles from 5	2.70	1.96
7. Water-solubles from 5	0.96	0.84
8. Hence water-solubles insol. in acetone	1.81	1.57
9. Acetone extract of NaOH-treated latex	1.70	1.45
10. Ether-solubles from 9	1.06	0.80
11. Water-solubles from 9	0.64	0.64
12. Hence acetone-solubles held back by NaOH	1.96	1.35
13. Ether-solubles of 12	1.63	1.16
14. Water-solubles of 12	0.33	0.19
15. Ether-soluble acids (free)		
Acid value	1.59	1.11
16. Ether-soluble saponifiables		
Sapon. value	0.76	0.98
17. Water-soluble acids		
Acid value	1.00	0.79
18. Total nitrogen	0.35	0.22
19. Protein nitrogen (in extracted coagulum)	0.22	0.13
20. Alcohol and water-soluble nitrogen	0.13	0.09
21. Acetone-soluble nitrogen	0.04	0.02
22. Non-ammonia nitrogen (NaOH-treated film)	0.32	0.21
23. Hence ammonia nitrogen	0.03	0.01
24. Ether-soluble nitrogen	0.015	0.009
25. Total ash	0.40	0.37
26. Magnesium in ash	0.002	0.001
27. Total phosphorus	0.041	0.035
28. Water-soluble phosphorus	0.018	0.018
29. Ether-soluble phosphorus	0.0006	0.0005
30. Protein phosphorus (in coagulum)	0.017	0.011
31. Acetone-soluble phosphorus	0.001	Nil

COMPARISON OF ELECTRODECANTED AND CENTRIFUGED CONCENTRATES

Comparative analysis of an electrodecanted and centrifuged concentrate gave the results in Table 3. The two concentrates were made from a common field latex, under experimental conditions. The results show a larger amount in the electrodecanted concentrate of some, but not all, nonrubber components. Because of the higher efficiency of the electro-decantation process, the concentrate contains more small rubber particles than the centrifuged concentrate, and hence contains a larger amount of rubber/serum interface material. The non-rubber components found in excess in the electrodecanted concentrate can, therefore, be tentatively classified as interface material, although there is the possibility that some ionic constituents may be concentrated with the rubber by electromigration.

The percentages in Table 3 are calculated on the dry film weight.

The electrodecanted concentrate contains a greater amount of ether-soluble acids (lines 13 and 15), nitrogen in all forms (lines 18-24), phosphorus (line 27) particularly protein phosphorus (line 30), and to a smaller extent water-solubles (line 4), particularly the acidic acetone-soluble portion held back by soda (line 14).

The ratio of these components in the two concentrates varies from 1.3:1 to 1.6:1; in many cases it is about 1.5:1. The consistency of this ratio in itself suggests a single underlying factor, such as the surface area ratio. The lower ratio found for water-soluble acids might indicate a less definite attachment of these fractions to the rubber/serum interface. On this assumption, the rubber/serum interface components are protein, including phosphoprotein, ammonium soaps of ether-soluble acids, choline (ether- and acetone-soluble nitrogen), and simpler protein structures and amino acids that are soluble in alcohol.

With the exception of the ether-solubles, the nonrubber components which are constant for the two concentrates belong to the serum. The nonacid water-soluble part of the acetone extract (line 11), which is mainly quebrachitol, is an example. Ash components (line 25) show a much smaller ratio, indicating that the mineral substances belong mainly to the serum.

The ammonia nitrogen contents of the two concentrates (line 23) show by inference that the electrodecanted concentrate contains a greater excess of acid over its metal content, amounting possibly to about 0.2 per cent, depending on the equivalent of the acid. This may be the result of the concentrating of anions with the negatively charged rubber particles.

The disposition of the nonrubber components was further elucidated by analysis of the electrodecanted latex serum, shown in Table 4.

The cation exchanger Zeokarb-225 retains amino acids and some of the peptide molecules; the resin Zeokarb-215 retains a small amount of nitrogenous material which passes through Zeokarb-225; passage through the anion-exchanger Deacidite-FF and then through Zeokarb-215 removes all nitrogenous material and virtually all the phosphorous-containing compounds.

Comparison of Table 4 with Table 3 shows large decreases of ether-solubles, alcohol-insoluble nitrogen and total phosphorus, showing that these substances are mainly attached to the rubber particles. Other components, such as water-solubles, including water-soluble phosphorus, ash, and soluble nitrogen compounds belong to the serum.

In order to verify that the difference between the electrodecanted and centrifuged concentrates lies in the rubber particle surface area, each of the latex

concentrates was diluted and centrifuged, keeping conditions near to those of the original centrifuging. This procedure should remove from the electrode-canted concentrate the small rubber particles which have already been removed from the centrifuged concentrate, and thus equalize the amounts of interface material. The results in Table 5 show that the additional interface material in the electrode-canted concentrate is, in fact, removed. The amounts of ether-soluble material including acids, water-solubles including acids, total nitrogen and protein nitrogen, are approximately constant for the two concentrates after centrifuging.

TABLE 4
ANALYSIS OF ELECTRODECANTED LATEX SERUM

	Per cent
1. Total solids	4.55
2. Total alcohol and water-solubles	3.44
3. Ether-solubles from 2	0.06
4. Water-solubles from 2	3.38
5. Protein from total non-ammonia nitrogen	0.31
6. Rubber (by difference)	0.80
7. Ash	0.29
8. Total nitrogen	0.17
9. Ammonia nitrogen	0.04
10. Nitrogen in alcohol and water-solubles	0.08
11. Alcohol-insoluble nitrogen	0.05
12. Total phosphorus	0.020
13. Water-soluble phosphorus	0.019
14. Phosphate phosphorus	ca. 0.004
15. Phosphate phosphorus after hydrolysis	0.014
16. Cationic material retained on Zeokarb-225	0.52 ^a
17. Anionic material retained on Deacidite-FF	0.98
18. Nonionic material unretained by resins	1.94 ^b
19. Amino acids	ca. 0.2

^a Unretained nitrogen, 0.007 per cent.

^b Phosphorus content, 0.001 per cent.

The above percentages are calculated on the serum weight.

INTERFACE MATERIAL AT THE TIME OF CONCENTRATING

The presence in electrode-canted concentrate of an excess of both protein and the phospholipin hydrolysis products shows that both phospholipin and soap were at the interface when the latex was concentrated. The phospholipin has however, at this time been partially hydrolyzed to form soap, as shown by the presence of choline and combined phosphate in electrode-canted serum, and soap has been found by Baker⁴ to replace protein at the interface.

The excess of both phospholipin and protein confirms the view of Cockbain²¹ that the protein is linked to the phospholipin, rather than to the rubber itself. This view is also shown by Smith¹² to provide an explanation for the mechanism of the enzymic decomposition of lecithin in latex. Hydrolysis of the phospholipin to soap disrupts the protein attachment, causing a release of protein into the serum, together with choline and glycerophosphate; probably a part of the choline is retained at the interface, competing with the ammonium ions for attachment to the fatty acid.

DISTRIBUTION OF NONRUBBER COMPONENTS BETWEEN SERUM AND RUBBER/SERUM INTERFACE

The quantitative distribution of nonrubber components in a field latex was calculated from analysis figures of the field latex and its electrode-canted serum, Tables 4 and 6.

TABLE 5
ANALYSIS OF ELECTRODECANTED/CENTRIFUGED AND DOUBLE
CENTRIFUGED CONCENTRATES

	Electro- decanted/ centrifuged (per cent)	Double centrifuged (per cent)
1. Total alcohol and water-solubles	2.74	2.80
2. Ether-solubles from 1	1.90	1.90
3. Water-solubles from 1	0.84	0.90
4. Acetone extract	2.22	2.17
5. Ether-solubles from 4	1.86	1.82
6. Water-solubles from 4	0.36	0.35
7. Total nitrogen	0.15	0.14
8. Nitrogen in alcohol and water-extracted coagulum	0.13	0.11
9. Acid value of ether-solubles	1.34	1.14
10. Sap. value of ether-solubles	1.6	1.6

mg. KOH
per g.
total solids

The above percentages are calculated on the total solids weight.

The percentage of serum in the field latex amounts to:

$$100 - S + \left(\frac{100 - S}{100} \times s \right)$$

where S = Percentage by weight total solids of field latex, and s = Percentage by weight total serum nonrubber components.

In the sample examined this amounts to 70.6 per cent. The serum nonrubber components in the field latex are, therefore, obtained by multiplying the analysis figures for the serum by 0.706, and the interface material is obtained by difference. The distribution of nonrubber components in the field latex is shown in Table 7.

The ether-solubles are seen to be rubber phase and interface material, and the water-solubles mainly, but not entirely, serum material. The nonionic material of the field latex serum amounts to 70.6 per cent of 1.94 per cent

TABLE 6
ANALYSIS OF FIELD LATEX FROM WHICH SERUM WAS OBTAINED

	Per cent
1. Total solids	32.0
2. Total alcohol and water-solubles	3.40
3. Ether-solubles from 2	0.60
4. Water-solubles from 2	2.80
5. Acetone extract	1.36
6. Ether-solubles from 5	0.73
7. Water-solubles from 5	0.63
8. Acetone extract of NaOH-treated film	0.73
9. Ether-solubles from 8	0.37
10. Water-solubles from 8	0.36
11. Hence ether-solubles held back by NaOH	0.36
12. Hence water-solubles held back by NaOH	0.27
13. Total nitrogen	0.17
14. Protein nitrogen (in extracted coagulum)	0.09
15. Ash	0.26
16. Total phosphorus	0.023
17. Magnesium	0.009

The above percentages are calculated on the latex weight.

(Table 4), or 1.36 per cent; subtraction of this nonionic material from the 2.39 per cent of serum water-solubles leaves 1.03 per cent of ionic material in the serum phase.

Nitrogen compounds are fairly evenly distributed between serum and rubber. The serum nitrogen can be split into 0.04 per cent as protein and 0.05 per cent as nonprotein, including amino acids and choline; the rubber nitrogen is 0.05 per cent protein and 0.03 per cent nonprotein, the latter probably being a mixture of degraded protein and choline.

Phosphorus compounds are also fairly evenly distributed between rubber and serum. The serum phosphorus consists of 0.003 per cent as free phosphate, 0.010 per cent as combined phosphate, and 0.001 per cent as phosphoprotein.

The rubber phase phosphorus contains most of the phosphoprotein, amounting to 0.005 per cent (calculated from the electrodecentrated concentrate) and 0.004 per cent of phospholipin phosphorus. On these calculations, it appears that the phospholipin, assumed in the fresh latex to be entirely in the rubber phase, is about 30 per cent unhydrolyzed at the time of the electrodecentration.

TABLE 7
DISTRIBUTION OF NONRUBBER COMPONENTS OF FIELD LATEX BETWEEN
SERUM AND RUBBER

	Field latex (per cent)	Serum phase (per cent)	Rubber phase (per cent)
1. Total solids	32.0	2.75	29.2
2. Total alcohol and water-solubles	3.40	2.43	0.97
3. Ether-solubles from 2	0.60	0.04	0.56
4. Water-solubles from 2	2.80	2.39	0.41
5. Non-ammonia nitrogen	0.17	0.09	0.08
6. Protein nitrogen (in extracted coagulum)	0.09	0.04	0.05
7. Phosphorus	0.023	0.014	0.009
8. Ash	0.28	0.21	0.05

The above figures represent percentages of the field latex.

The ash components are mostly in the serum, and since the metal ions are attached to the stronger of the acids available, these too are mainly in the serum. Mineral salts of the water-soluble acids account for twice the ash weight, since the equivalent of the acids is about 120. This amounts to about 0.4 per cent in a total of 1.0 per cent of ionic material. The acids in the form of ammonium salts account for 10 times the ammonia nitrogen weight or 0.4 per cent of the latex; the remaining 0.2 per cent of ionic material contains the amino acids and other serum noncoagulable nitrogen compounds.

RATIO OF RUBBER/SERUM INTERFACE MATERIAL IN ELECTRODECANTED AND CENTRIFUGED CONCENTRATES

From the total solids figures for the electrodecentrated concentrate (Table 3), serum (Table 4), and field latex (Table 6), it can be shown by calculation on the lines already indicated that the electrodecentrated concentrate already analyzed (Table 3) contains 2.1 times the rubber phase components and 0.55 times the serum components of the field latex. On this basis, a calculated reconstruction of such a concentrate has been made, the total nonrubbers being then compared with the analytical results from Table 3, expressed on the latex weight by multiplying by $\frac{62.8}{100}$.

The concentrate was not made from the field latex analyzed, but was obtained from the same seedling stock; this circumstance may be responsible for differences between calculated and actual figures. The higher theoretical water-solubles figure may also arise from the concentrating of serum components with the rubber, the impoverishment of the serum more than counterbalancing the enrichment of the rubber phase. This effect, if operative at all, can only be small, as there is such close agreement after electrodecaned and centrifuged concentrates have been diluted and centrifuged (Table 5).

More reliance may be placed on the figures for serum and interface where the calculated total shows reasonable agreement with the actual figure.

Once the amount of a component in the serum has been correctly evaluated for the electrodecaned concentrate, deduction of this amount from the corresponding total value gives the amount of interface material for the centrifuged concentrate. Thus a ratio of interface material for the two concentrates is obtained, which is a measure of their relative rubber particle surface areas.

TABLE 8
CALCULATED DISTRIBUTION AND ACTUAL FIGURES FOR THE NONRUBBER
COMPONENTS OF ELECTRODECANTED LATEX

	Serum phase (per cent)	Rubber phase (per cent)	Calculated total (per cent)	Actual total (per cent)
1. Total solids	1.52	61.1	62.6	62.6
2. Total alcohol and water-solubles	1.34	2.04	3.38	3.16
3. Ether-solubles from 2	0.02	1.17	1.19	1.43
4. Water-solubles from 2	1.31	0.87	2.18	1.73
5. Ether-solubles from acetone extract	0.04	1.45	1.49	1.69
6. Non-ammonia nitrogen	0.05	0.17	0.22	0.20
7. Ash	0.12	0.10	0.22	0.25
8. Phosphorus	0.008	0.019	0.027	0.026

The above percentages are calculated on the latex weight.

In the preceding analysis there are several factors which reduce the reliability of this ratio; a more likely assessment could be made from analyses of a field latex, the electrodecaned and centrifuged concentrates obtained directly from it, and its freeze-dried serum.

SUMMARY

Analyses of ammonia-preserved latex concentrates have been made in order to study some of the main features of composition of the nonrubber material at the time of using the latex, usually about three months after tapping on the plantations. The information thus obtained is supplementary to corresponding work carried out on fresh latex in Malaya.

Latex, at the stage now being considered, contains no phospholipin as such; but its decomposition products, ammonium soaps, free choline, and combined phosphate (probably glycerophosphate) are found. There is protein in the serum and at the rubber interface, a small amount of free amino acid, and probably also substances of a polypeptide nature. The serum contains salts of volatile and nonvolatile acids, in some cases as ammonium salts, and also a considerable amount of quebrachitol. The rubber phase contains phytosterol esters.

From the analyses of an electrodecanted and a centrifuged concentrate prepared from a common field latex it is shown that the higher amounts of some, but not all, nonrubber components in the electrodecanted concentrate are in accordance with its having a smaller average rubber particle size. The excess of both protein and phospholipin breakdown products indicates the existence of a protein-phospholipin complex.

Analysis of the serum remaining after electrodecantation and of the original field latex has enabled a tentative distribution of nonrubber material to be calculated between serum and rubber phases.

ACKNOWLEDGMENT

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THE PLASTICIZATION OF RUBBER ON ROLL MILLS

EUGENE STALINSKY

RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 28, No. 4, pages 1005-1006, October-December 1954, contains an article entitled "The Plasticization of Rubber on Roll Mills".

At the top of page 1006, the text reads:

It was further established that the relation between p and N is of the form:

$$p = K\sqrt{N} + p_0$$

This equation is incorrect, and should be:

$$p = \frac{K}{\sqrt{N}} + p_0$$

This equation is correctly recorded in a paper by the same author on the "Energy Consumed in the Plasticization of Rubber on a Roll Mill", in this issue of RUBBER CHEMISTRY AND TECHNOLOGY, pages 606-607.

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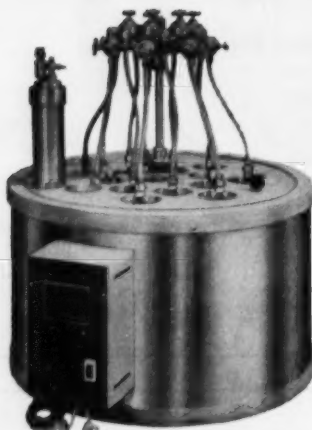
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